278. The Course of the Catalytic Hydrogenation/Isomerization Reaction of Steroidal Ring B Olefins in the 13β- and 13α-Series[1])

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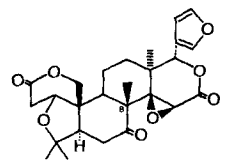
In memoriam *Louis F. Fieser*

(1.X.79)

Summary

The course of the catalytic hydrogenation and isomerization (H_2/*Raney*-Ni/dioxane or H_2/Pd/C/EtOH) of $\Delta^{5,7}$-, Δ^{7}-, Δ^{8}-, and $\Delta^{8(14)}$-steroid olefins was shown to depend strongly on the configuration at C(13). The known hydrogenation/isomerization of reactions of $\Delta^{5,7}$-dienes in the 13β-series to Δ^{7}-(H_2/*Raney*-Ni/dioxane) and $\Delta^{8(14)}$-olefins (H_2/Pd/C/EtOH) were also confirmed in the 3β,19-epoxy-13β- and 3-Oxo-19-acetoxy-13β-steroid series (*e.g.* **32**→**35**→**37**, *Scheme 3*). On the other hand, in the corresponding 13α-steroid series the same reactions afforded the Δ^{7}-, and the Δ^{8}-olefins (mixture of products with H_2/*Raney*-Ni/dioxane; quantitatively the Δ^{8}-compounds with H_2/Pd/C/EtOH; s. *e.g. Scheme 3*). A similar dependence on the C(13) configuration was observed in the allylic oxidation of these olefins with SeO_2 (*Fieser*'s test, see *Table*), and in the acid catalyzed opening of the 7α,8α-epoxides (*e.g.* **60**→**62**+**63** in the 13β-series, and **56**→**64**+**65** in the 13α-series, *Scheme 8*).

1. Introduction. – In connection with our studies directed towards a partial synthesis of limonin (**i**) [1] we intend to introduce the requisite 8β-angular methyl group into the steroid skeleton by a stereoselective, intramolecular alkylation. For this purpose we examined routes starting from compound **1** *(Scheme 1)*



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[1]) Part of the Ph.D. thesis ETHZ of *G.A.*, in preparation.

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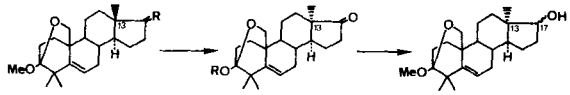
[2] to suitable ring B functionalized 13α-steroid derivatives. The results of these investigations described below show clearly that especially the olefin isomerization in the B/C/D ring moiety and the acid catalyzed rearrangement of 7α,8α-epoxides are strongly influenced by the configuration at C(13).

2. Preparation of the $\Delta^{5,7}$-13α-diene 12 *(Scheme 3).* – The 13β-ketone **2** was converted into the corresponding 13α-ketone **5** by the method of *Barton et al.* [3] (treatment of the oxime **3** with pyridine/Ac_2O) in an overall yield of 60% (**2**→**5**). Reduction of the 17-oxo function of **5** with $LiAlH_4$ in THF or with

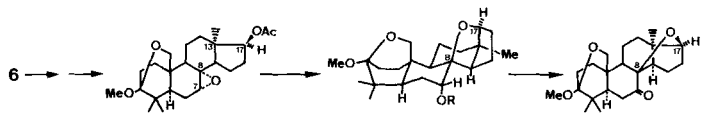
Scheme 1



$NaBH_4$ in MeOH/H_2O gave the two epimeric alcohols **6** (17β-OH) and **7** (17α-OH) in a ratio of 1:3. Using the sterically demanding reducing reagent LiAl (t-pentyloxy)$_3$H in refluxing dioxane yielded **6** and **7** in a ratio of 7:2 (see also [4]). The configuration at C(17) of **6** and **7** was assigned by the empiric rule of *Bose & Chatterjee* [5][2]), and was later confirmed by the synthesis of the compounds **8**–**10** from **6** *(Scheme 2):* an O-bridge from C(17) to C(8) is possible only in 17β-hydroxy-13α-steroids.

The $\Delta^{5,7}$-13α-diene **12** *(Scheme 3)* was obtained in 65% yield from **11**[3]), the acetyl derivative of **6**, by allylic bromination with 1,3-dibromo-5,5-dimethylhydantoine in refluxing benzene/hexane followed by dehydrobromination (s. *e.g.* [8–10]).

Scheme 2



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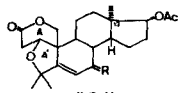
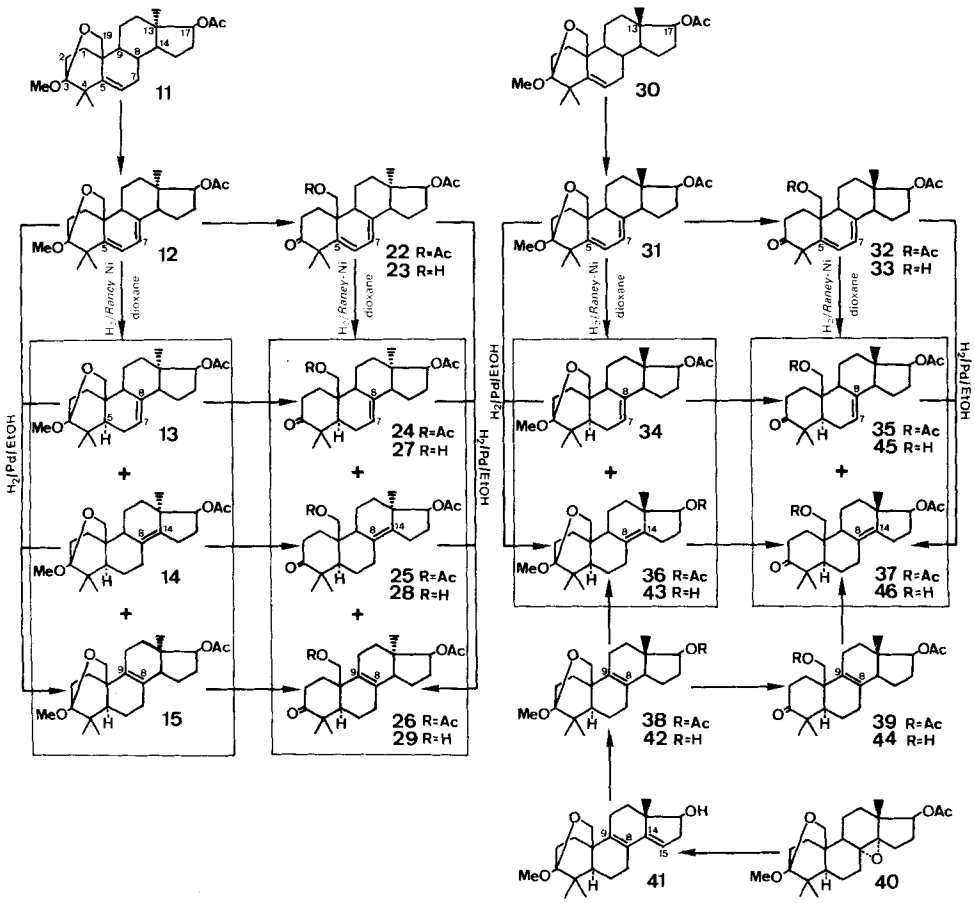
2) According to the empiric rule of *Bose & Chatterjee* [5] 13α-steroids with a 17β-OR substituent must be more dextrogyr than the ones with a 17α-OR substituent. In the present work exceptions of this rule were found: **12** (+400°) and **19** (+533°), **15** (+43°) and **21** (+96°), and **56** (−25°) and **57** (−23°). (For an alternative method of determination of these configurations see [6] [7].)

3) **ii** and **iii** with the partial structure A/A′ of limonin (**i**) and with 13α-configuration were synthesized from **11** in 9 and 11 steps, in overall yields of 27% and 18%, respectively [11].

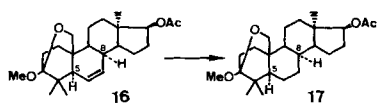


3. Hydrogenation of the $\Delta^{5,7}$-, Δ^{7}-, and $\Delta^{8(14)}$-13α-steroids 12, 13, and 14, respectively. – Hydrogenation of the $\Delta^{5,7}$-13α-diene **12** *(Scheme 3)* in dioxane with *Raney*-nickel as a catalyst gave in addition to the expected Δ^{7}-olefin **13** (55%) and the $\Delta^{8(14)}$-olefin **14** (7%) surprisingly[4]) the Δ^{8}-isomer **15** (26%)[5]). Moreover, **16** and **17** *(Scheme 4)* were obtained in amounts of 5% each.

Scheme 3



Scheme 4



[4]) Hydrogenation of $\Delta^{5,7}$-13β-dienes under the same conditions (s. *e.g.* [12] [13]) always yielded as the main product the Δ^{7}-compound and to a smaller amount the $\Delta^{8(14)}$-isomer. The Δ^{8}-olefin was never observed.

[5]) For determination of the double bond position s. chap. 10.

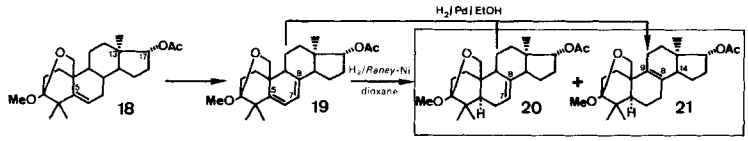
The 5α-configuration of all hydrogenation products was proved by ^{1}H-NMR. spectroscopy: The *long-range W-coupling* in the *A*- and *B*-part of the *AB*-system of 2 H–C(19) is consistent only with the 5α-configuration [2].

It is known (s. *e.g.* [12] [13]) that treatment with H_2/Pd/C in EtOH of $\Delta^{5,7}$-dienes, as well as of Δ^7- and Δ^8-steroid olefins in the 13β-series leads to the $\Delta^{8(14)}$-compounds. In marked contrast the diene **12** as well as the Δ^7-olefin **13** and the $\Delta^{8(14)}$-olefin **14** in the 13α-series afforded under these conditions the Δ^8-olefin **15** *(Scheme 3)* in quantitative yield.

These in steroid chemistry unusual isomerizations must be due to the steric influence of the 17β-acetoxy function or to a particular strain in the steroid skeleton. This strain may be the result of the bridging acetal system in ring A or of the 13α-configuration. The results of the hydrogenation of the 17α-acetoxy compounds **19** and **20** (s. chap. 4 and *Scheme 5*), of the 3-oxo-19-acetoxy-13α-olefins **22**, **24** and **25** (s. chap. 5 and *Scheme 3*), and of the corresponding 13β-isomers (s. chap. 6 and *Scheme 3*) will show that the H_2/Pd catalyzed isomerization of Δ^7-, Δ^8-, and $\Delta^{8(14)}$-double bonds is strongly influenced by the configuration at C(13) (*cis*- or *trans*-anellation of rings C and D, cf. chap. 11).

4. The course of the hydrogenation of the 17α-acetoxy-$\Delta^{5,7}$-13α-diene 19. – The diene **19**[6]) (17α-OAc) in the 13α-series *(Scheme 5)* afforded on hydrogenation with *Raney*-nickel in dioxane the Δ^7- and Δ^8-olefins **20** and **21**, in a ratio of 3:1[5]). The diene **19** and the Δ^7-olefin **20** on hydrogenation with Pd/C in EtOH quantitatively afforded the Δ^8-steroid **21**. The olefinic $\Delta^{8(14)}$-isomer could not be isolated nor detected in this reaction.

Scheme 5



5. The course of the hydrogenation of the 3-oxo-19-acetoxy-$\Delta^{5,7}$-13α-diene 22. – The diene **22**[7]) *(Scheme 3)* in the 13α-series afforded on hydrogenation with *Raney*-nickel in dioxane the isomeric olefins **24**–**26** *(Scheme 3)*[8]). The ratio 8:1:4 of these olefins corresponded to the ratio obtained on hydrogenation (*Raney*-nickel/dioxane) of **12** *(Scheme 3)*.

Treatment of the 13α-compounds **22**, **24**, and **25**, respectively, in EtOH with H_2 and Pd/C afforded in quantitative yields the Δ^8-13α-olefin **26**.

The ketones **24**–**26** were correlated with the corresponding acetals **13**–**15** by acid hydrolysis of the latter (→ **27**–**29**) and acetylation.

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[6]) Prepared by acetylation of **7** *(Scheme 1)*, followed by allylic bromination of the resulting **18** and dehydrobromination.

[7]) Compound **22** was obtained from **12** by acetal cleavage ($HOAc/H_2O$) giving **23**, and acetylation (Ac_2O/pyridine).

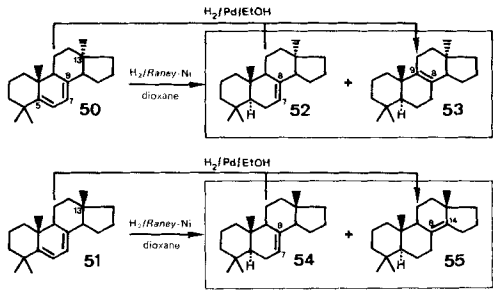
[8]) On hydrogenation the 3-oxo function was reduced to the alcohol. The mixture was reoxidized (Pyridinium-chlorochromate, CH_2Cl_2).

6. Examination of the hydrogenation of olefins in the 13β-series. – The $\Delta^{5,7}$-13β-steroids **31**[9]) and **32**[10]) afforded on hydrogenation with *Raney*-nickel in dioxane as expected[4]) predominantly the Δ^{7}-compounds **34** and **35**, respectively, each in 94% yield *(Scheme 3)*. Minor amounts of the isomeric $\Delta^{8(14)}$-olefins **36** and **37**[5]), respectively, were obtained. The isomeric Δ^{8}-olefins **38** and **39**, respectively, could not be detected and had to be synthesized from **36** by epoxydation with *m*-chloroperbenzoic acid (→**40**), followed by treatment with MeOH/HCl (→**41**), partial hydrogenation of the diene system in dioxane with *Raney*-nickel (→**42**)[11]), acetylation (→**38**), acetal cleavage (→**44**), and reacetylation (→**39**).

Treatment of the $\Delta^{5,7}$-13β-diene systems **31** and **32**, of the Δ^{7}-13β-olefins **34** and **35**, and of the Δ^{8}-13β-compounds **38** and **39** in EtOH with H_2 and Pd/C yielded quantitatively the $\Delta^{8(14)}$-compounds **36** and **37**, respectively *(Scheme 3)*. The acetals **34** and **36** were correlated with the ketons **35** and **37**, respectively, by hydrolysis (→**45** and **46**) and acetylation.

7. Examination of the hydrogenation of the olefins 50–52 and 54 *(Scheme 6)*. – To make definitively sure that the isomerization described above is not influenced by the oxygen-bearing substituents and only dependent on the C(13)-configuration, the 13α- and 13β-4,4-dimethyl-5,7-androstadienes (**50** and **51**) were synthesized[12])

Scheme 6



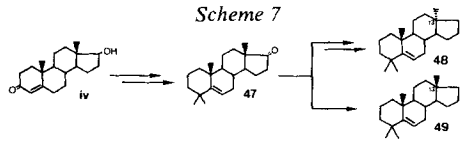
[9]) Prepared by acetylation of **1** *(Scheme 1)*, allylic bromination of the intermediate **30** and dehydrobromination.

[10]) Prepared by acetal cleavage of **31** *(Scheme 3)* giving **33** and acetylation.

[11]) Under these hydrogenation conditions small amounts of the 1,4-addition product **43** ($\Delta^{8(14)}$) were formed.

[12]) **50** and **51** were synthesized by known reaction sequences starting from testosterone **iv** *(Scheme 7)*. Dimethylation [9] [14], *Wolff-Kishner* reduction [9] [15] and *Jones* oxidation gave **47** [9]. Epimerization at C(13) (65% yield) according to the method of *Barton et al.* [3] and *Wolff-Kishner* reduction led to the unsaturated 13α-hydrocarbon **48**. (For the preparation of this compound we thank *Max Züger*, teaching laboratories in organic chemistry at ETHZ, summer 1979). **49** [9] [16] was available by *Wolff-Kishner* reduction of **47**. The dienes **50** and **51** [9] *(Scheme 6)* were prepared from **48** and **49**, respectively, by allylic bromination with 1,3-dibromo-5,5-dimethylhydantoine followed by dehydrobromination.

Scheme 7



and hydrogenated. In dioxane with H_2 and *Raney*-nickel the 13*α*-compound **50** afforded a mixture of the Δ^7- and the Δ^8-olefins **52** [17] and **53** *(Scheme 6)* in a ratio of 4:1 (^{1}H-NMR.-integration). Under the same conditions the 13*β*-compound **51** afforded as expected[4]) a 6:1 mixture of the Δ^7- and the $\Delta^{8(14)}$-olefins **54** and **55**[13]). Treatment of the 13*α*-compounds **50** ($\Delta^{5,7}$) and **52** (Δ^7) in EtOH with H_2 and Pd/C led quantitatively to the Δ^8-olefin **53**[5]). The corresponding 13*β*-compounds **51** ($\Delta^{5,7}$) and **54** (Δ^7), respectively, led under the same conditions to the $\Delta^{8(14)}$-olefin **55**[5])[13]).

The hydrogenation and isomerization reactions of olefins described in chap. 3–7 in the 13β- and 13α-steroid series clearly show that the course of the reaction is strongly dependent on the C(13)-configuration (s. discussion, chap. 11).

8. *Fieser*'s selenium dioxide test. – The selenium dioxide test [18][14]) was carried out with the $\Delta^{5,7}$-, Δ^7-, and $\Delta^{8(14)}$-steroid derivatives in the 13*α*- and 13*β*-series. The results are summarized in the *Table*. The olefins of the 13*β*-series followed the rules given by *Fieser*. In the 13*α*-series the $\Delta^{5,7}$-dienes **12**, **22** *(Scheme 3)*, **19** *(Scheme 5)*, and **50** *(Scheme 6)*, and the Δ^7-compounds **13**, **24** *(Scheme 3)*, **20** *(Scheme 5)*, and **52** *(Scheme 6)* showed, as expected, a *positive* reaction with SeO_2 (see *Table*). Because of the *negative* results given by the Δ^8-13*α*-compounds **15**, **26** *(Scheme 3)*, **21** *(Scheme 5)*, and **53** *(Scheme 6)* having all the required allylic 14*α*-H-atom[15]), and because of the positive results shown by the $\Delta^{8(14)}$-13*α*-compounds **14** and **25** bearing an allylic 9*α*-H-atom, it is unlikely that the 14*α*-H-atom is the site of SeO_2 attack in the 13*α*-series. The enhanced sensitivity of the allylic 9*α*-H-atom as compared with the allylic 14*α*-H-atom in the 13*α*-series[15]) correlates with the course of the above described catalytic isomerization in the 13*α*-series.

Table. Fieser*'s selenium dioxide test.*

Structure of ring A	Structure of ring B/C			
	Configuration at C(13)				
	13*β*	**31**: +	**34**: +	**36**: –	**38**: +
	13*α*	**12**: +	**13**: +	**14**: +	**15**: –
		19: +	**20**: +	-	**21**: –
	13*β*	**32**: +	**35**: +	**37**: –	**39**: +
	13*α*	**22**: +	**24**: +	**25**: +	**26**: –
	13*β*	**51**: +	**54**: +	**55**: –	-
	13*α*	**50**: +	**52**: +	-	**53**: –

[13]) For other preparations of **55** s. [9] [16].

[14]) Low temperature (25°) oxidation by selenium dioxide is specific to steroids of the 5*α*- and Δ^5-series with an allylic 14*α*-H-atom as in $\Delta^{5,7}$-, $\Delta^{6,8}$,$\Delta^{7,9(11)}$-dienes and in Δ^7, and Δ^8-olefins. The test is feasible for the detection of small quantities of these olefins, and when positive a yellow coloration develops, followed by separation of a red precipitate of selenium.

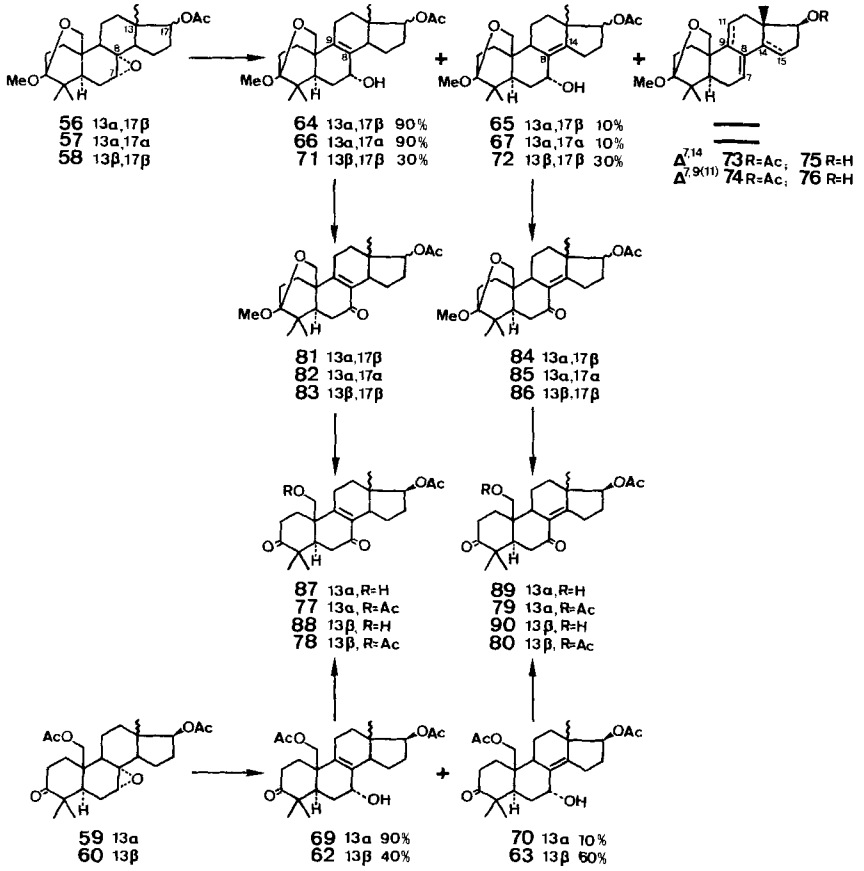
[15]) *Fieser*'s results [18] indicate that an allylic 9*α*-H-atom does not exhibit the sensitivity of a 14*α*-H-atom towards SeO_2.

9. Acid catalyzed opening of 7α,8α-epoxides. – The Pd/H_2 catalyzed isomerization of Δ^7-, and $\Delta^{8(14)}$-double bonds into the Δ^8-position in 13α-steroids prompted us to investigate the acid catalyzed opening of 7α,8α-epoxides in likewise functionalized 13α- and 13β-steroids. It is known [19] [20] that 7α,8α-epoxides of the 13β-series predominantly afford the $\Delta^{8(14)}$-allylic alcohols (type **v**) together with small amounts of the Δ^8-compounds (type **vi**). In the following it is shown that 7α,8α-epoxides of the 13α-series afford, in contrast to the 13β-compounds, by treatment with $CHCl_3$/HCl predominantly the Δ^8-allylic alcohols (type **vi**).

v **vi**

The epoxides **56**–**60** *(Scheme 8)* have been synthesized from the corresponding Δ^7-olefins **13**, **24**, **34**, **35** *(Scheme 3)* and **20** *(Scheme 5)* by *m*-chloroperbenzoic acid

Scheme 8



oxidation in ether. The yield was quantitative in the cases of **56**, **57**[16]), **58** and **59**. However the 7*α*,8*α*-epoxide **60** in the 13*β*-series could not be isolated. After chromatographic purification of the reaction mixture the Δ^8- and $\Delta^{8(14)}$-allylic alcohols **62** and **63**[5]), respectively, were obtained directly in a ratio of 4:6 *(Scheme 8)*.

Acid treatment ($CHCl_3$/HCl) of the 7*α*,8*α*-epoxides **56**, **57** and **59** of the 13*α*-series for 15 minutes generated in quantitative yields the mixtures of the Δ^8- and $\Delta^{8(14)}$-allylic alcohols **64/65**, **66/67**[17]), and **69/70**, respectively, each in a ratio of 9:1 *(Scheme 8)*.

On treatment of the 7*α*,8*α*-epoxide **58** (13*β*-series) under the same acidic conditions only 50% of **58** were converted. The products isolated in about equal quantities were the Δ^8- and $\Delta^{8(14)}$-allylic alcohols **71** and **72** and a 1:7 diene mixture[18]) **73/74**[19]), respectively.

In both series (13*α* and 13*β*) the Δ^8- (**64** and **71**) and the $\Delta^{8(14)}$-3,19-epoxy-allylic alcohols (**65** and **72**), were correlated with the corresponding 19-acetoxy-3-oxo-allylic alcohols (**69**, **62** and **70**, **63**, respectively) by the relay compounds **77**–**80** (s. *Scheme 8*). The relay compounds were obtained from the 3,19-epoxy-steroids by oxydation with pyridiniumchlorochromate in CH_2Cl_2 (→**81**, **83**, **84** and **86**), acetal cleavage with AcOH/H_2O (→**87**–**90**) and acetylation.

The preferential rearrangement of the 7α,8α-epoxides in the 13α-series to Δ^8-allylic alcohols also confirms the influence of the configuration at C(13) on this reaction course.

10. Determination of the double bond position. – *13α-steroids.* The position of the double bond in the isomerization products has been proved by RuO_4-cleavage [21] of the olefinic bond (s. *Scheme 9*). Δ^8-double bonds afforded the 10membered ring diketones **91**–**93** which show carbonyl absorption bands at 1696, 1694 and 1688 cm^{-1}, respectively, [21]. The cleavage of the $\Delta^{8(14)}$-double bond in **14** yielded the dicarbonyl compound **94** [IR.: 1713 (6membered ring ketone); *ca.* 1735 cm^{-1} (5membered ring ketone, covered by the acetate carbonyl); however, the latter band is clearly recognizable at 1735 cm^{-1} in the 17-hydroxy compounds **95** and **96**].

13β-steroids. The olefinic bond in **38** (Δ^8), **36** ($\Delta^{8(14)}$ *(Scheme 3)*, and **55** $\Delta^{8(14)}$, *(Scheme 6)* was located by comparing the $H_3C(18)$ resonances in the ^{1}H-NMR. spectrum with the extensive data tabulated by *Zürcher* [22][20]). Moreover, the $\Delta^{8(14)}$-double bond assigned to **36** and **55** (13*β*-series)

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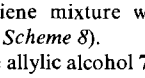
16) Epoxidation of the 17*α*-acetoxy-Δ^7-13*α*-compound **20** *(Scheme 5)* afforded in addition to the 7*α*,8*α*-epoxide **57** small amounts of the 7*β*,8*β*-epoxide **61**. These two epoxides can clearly be differentiated by ^{1}H-NMR. spectroscopy: 7*β*,8*β*-epoxide **61**: 3.06 (*d*×*d*, *J*=4, *J'*=3, H–C(7)); 7*α*,8*α*-epoxides **56** and **57**: 2.98 (broadened *t*, *J*≈2, H–C(7)). In addition, the large difference in the chemical shifts ($\Delta\delta$=0.67 ppm) of the 2 H–C(19) (*AB*-system) confirms the *β*-position of the oxirane ring in **61**. The corresponding difference in the 7*α*,8*α*-epoxides **56** and **57** is only 0.15 and 0.13 ppm, respectively. Compared with the 7*α*,8*α*-epoxides the 7*β*,8*β*-oxirane compound proved to be stable under acidic conditions (HCl/$CHCl_3$).



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17) Characterized as the 7*α*,17*α*-diacetoxy-derivative **68**.

18) Chromatographic separation of the diene mixture was successfully conducted after hydrolysis of the 17-acetoxy function (s. **75** and **76**, *Scheme 8*).

19) **74** was also obtained by treatment of the allylic alcohol **71** with $POCl_3$ in pyridine.

20) Thirty examples showed that an additional increment of −0.04 ppm must be considered in the case of the 3,19-epoxy-4,4-dimethyl-(type **vii**) as well as in 4,4-dimethyl-19-acetoxy-steroids (type **viii**).

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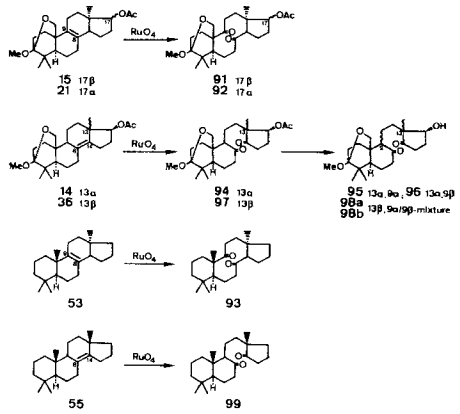
viii

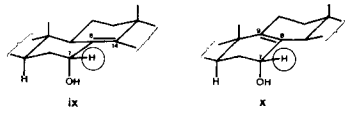
Scheme 9



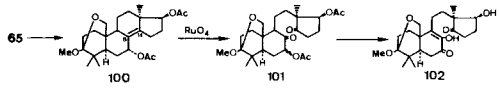
was confirmed by cleavage of the olefinic bond with RuO_4 giving **97** and **99**, respectively (s. *Scheme 9*). [IR. ($CHCl_3$) of **97**: 1735, 1715 cm^{-1}; IR. ($CHCl_3$) of **98a/98b**: 1735, 1715 cm^{-1}; IR. (CCl_4) of **99**: 1735, 1710 cm^{-1}.]

Allylic alcohols in the 13α- and 13β-series. In the 13β-series the isomeric Δ^8- (**62** and **71**) and $\Delta^{8(14)}$-allylic alcohols (**63** and **72**; *Scheme 8*) were distinguished according to the ^{1}H-NMR. chemical shifts of the $H_3C(18)$-signal [22][20]).

In addition to the evidence given above, the ^{1}H-NMR spectrum of the $\Delta^{8(14)}$-compounds (type **ix**), compared with the Δ^8-compounds (type **x**), showed the signal of the 7β-H-atom deshielded by 0.5 ppm under the influence of the $\Delta^{8(14)}$-double bond. This difference (0.5 ppm) in the chemical shift of the 7β-H-atom (**ix** *vs.* **x**) was used to assign the position of the Δ^8- and $\Delta^{8(14)}$-double bond, respectively, in the allylic alcohols of the 13α-series. Moreover, in the case of **65** *(Scheme 8)* the presence of the $\Delta^{8(14)}$-double bond was confirmed by cleavage of the olefinic bond in the corresponding acetoxy derivative **100** and saponification of the product **101** with K_2CO_3/MeOH to **102**[21]) (s. *Scheme 10*).



Scheme 10



11. Discussion. – The striking difference between the course of the catalytic isomerization reaction of the Δ^7-double bond in the 13β- and 13α-steroid series described in chap. 3–7 can be explained as follows: from the fact that the Δ^8-13α-olefins and the $\Delta^{8(14)}$-13β-olefins are position stable on prolonged H_2/Pd/C treatment (2 days, room temperature) it can be concluded that the olefins originally obtained are the products of thermodynamic control. That is, the direction of isomerization (Δ^8 *vs.* $\Delta^{8(14)}$) is due to the different release of strain in the products.

[21]) The primarily formed α-hydroxyketone was oxidized by air under the basic reaction conditions.

Model inspection indicates that the Δ^7-13β-olefins (C/D-*trans!*) on isomerization to the $\Delta^{8(14)}$-olefins lose much of their inherent strain, whereas the isomerization of the Δ^7-13α-olefins (C/D-*cis*) is not driven by such strain release on abstracting the allylic 14α-H-atom. The best process for the latter olefin must be the isomerization to the endocyclic Δ^8-position.

A satisfactory explanation of the reactivity differences of the respective olefins in the SeO_2 oxidation (*Fieser's* test) shown in the *Table* cannot be suggested at this time. Neither steric approach control of SeO_2[22]) nor the relative position of the allylic H-atom to the plane of the olefin can account for the selectivity observed in the oxidation.

Financial support by *Ciba-Geigy AG*, Basel, and by *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is greatfully acknowledged.

Experimental Part

General remarks s. [2].

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5-androsten-17-one (**2**) was obtained from **1** [2] by *Jones* oxidation in quantitative yield. M.p. 163°, $[\alpha]_D = +10°$ ($c = 1.36$). – IR.: 1735, 1382, 1332, 1126, 1085, 1060, 1034, 992, 970, 900. – ^{1}H-NMR.: 0.88 (*s*, $H_3C(18)$); 1.10 and 1.13 (2*s*, $2\,H_3C-C(4)$); 3.32 (*s*, CH_3O); 3.74 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 3.99 (*d*, $J = 8$, 1 H–C(19)); 5.60 (*d*×*d*, $J = 6$, $J' = 1$, H–C(6)). – MS.: *344* (M^+, 100), 329 (21), 301 (80), 269 (21), 220 (80).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5-adrosten-17-one oxime (**3**) was obtained in quantitative yield by treating **2** under reflux (2 h) with 0.6M hydroxylamin hydroacetate in methanol. M.p. 224°, $[\alpha]_D = -57°$ ($c = 1.09$). – IR.: 3580, 3280 br., 1670, 1380, 1332, 1128, 1090, 1034, 934, 914, 880. – ^{1}H-NMR.: 0.92 (*s*, $H_3C(18)$); 1.10 and 1.13 (2*s*, $2\,H_3C-C(4)$); 2.53 (*m*, 2 H–C(16)); 3.33 (*s*, CH_3O); 3.74 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 3.99 (*d*, $J = 8$, 1 H–C(19)); 5.58 (*d*×*d*, $J = 6$, $J' = 1.5$, H–C(6)); 8.68 (*s*, HON–C(17), exchangeable with D_2O). – MS.: *359* (M^+, 100), 344 (48), 343 (54), 342 (49), 328 (51), 327 (36), 316 (38).

$C_{22}H_{33}NO_3$ (359.49) Calc. C 73.50 H 9.25 N 3.96% Found C 73.50 H 9.17 N 3.89%

Thermal epimerization at C(13) [3], **3**→**4**→**5**. A solution of 4.72 g oxime **3** in 120 ml of dry pyridine and 120 ml of acetic anhydride was heated under reflux and under nitrogen for 16 h. The solvent was removed under reduced pressure, the residual black tar was taken up in ethyl acetate (50 ml) and ether (50 ml), and aqueous $NaHCO_3$-solution (50 ml) was added. The mixture was stirred vigorously for 2 h, then filtered through a *Celite* pad, which was washed thoroughly with ether. The organic layer was separated, washed with dilute HCl-solution, aqueous $NaHCO_3$-solution and brine, dried ($MgSO_4$), and evaporated. The residue was hydrolyzed by treating with acetic acid (100 ml) and water (30 ml) at 80° for 16 h. After normal work-up the crude product **4**[23]) was treated with anhydrous methanolic hydrochloric acid at RT. for 4 h. After work-up the crude product was chromatographed on silicagel (cyclohexane/ethyl acetate 9:1): 2.8 g (62%) of **5**[24]) and 0.26 g of starting material **2**.

3β,19-Epoxy-3α-hydroxy-4,4-dimethyl-13α-androst-5-en-17-one (**4**)[25]). M.p. 188–190°, $[\alpha]_D = -151°$ ($c = 4.15$). – IR.: 3590, 1725, 1450, 1435, 1405, 1375, 1356, 1318, 1288, 1135, 1122, 1090, 1078, 1065,

[22]) For a mechanistic proposal of the allylic SeO_2 oxidation see [23].

[23]) An analytical sample was chromatographed on silicagel with benzene/ethyl acetate 4:1 and recrystallized from acetone.

[24]) UV. irradiation of **2** in cyclohexane gave the desired 13α-product **5** in 28% yield (*ca.* 43% in terms of consumed starting material [4]).

[25]) S. footnote 11) in [2].

1035, 1008 sh., 975, 940, 910, 870, 853, 838. – ^{1}H-NMR.: 0.96 and 1.09 (2*s*, 3 H and 6 H, resp., 2 H_3C–C(4) and H_3C(18)); 3.50 (*d*×*d*, *J*=8, *J'*=3, 1 H–C(19)); 3.79 (*d*, *J*=8, 1 H–C(19)); 5.56 (*d*×*d*, *J*=7, *J'*=2, H–C(6)). – MS.: 330 (M^+, 70), *300* (100), 299 (32), 287 (36), 257 (42), 244 (31), 97 (56).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androst-5-en-17-one (**5**). M.p. 193–194°, $[\alpha]_D = -138°$ (*c*=1.23). – IR.: 1735, 1380, 1330, 1125, 1082, 1072, 1034, 1010, 968, 904. – ^{1}H-NMR.: 1.00, 1.09 and 1.10 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.31 (*s*, CH_3O); 3.56 (*d*×*d*, *J*=8, *J'*=3, 1 H–C(19)); 3.78 (*d*, *J*=8, 1 H–C(19); 5.58 (*d*×*d*, *J*=6, *J'*=2, H–C(6)). – MS.: *344* (M^+, 100), 329 (10), 301 (96), 269 (40).

$C_{22}H_{32}O_3$ (344.48) Calc. C 76.70 H 9.36% Found C 76.55 H 9.37%

Reduction **5**→**6** *and* **7**. a) A solution of 1.9 g (5.52 mmol) of **5** and 3.9 g of LiAl(*t*-pentyloxy)$_3$H in 30 ml of dioxane was heated under reflux for 2 h. The solution was poured into ice/dilute hydrochloric acid and extracted with ethyl acetate. The residue was chromatographed on silicagel (cyclohexane/ethyl acetate 3:1) giving 1.4 g (73%) of the 17*β*-compound **6** and 0.39 g (20%) of the 17*α*-compound **7**.

b) A solution of 2.0 g (5.81 mmol) of **5** in 20 ml of THF was treated at RT. with 1 g of $LiAlH_4$ for 3 h. Work-up and chromatography on silicagel yielded 0.463 g (23%) of **6** and 1.448 g (72%) of **7**.

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androst-5-en-17β-ol (**6**). M.p. 172–174°, $[\alpha]_D = -64°$ (*c*=0.75). – IR.: 3620, 1380, 1330, 1130, 1100, 1085, 1040, 1015, 992, 975, 945, 905. – ^{1}H-NMR.: 0.80, 1.06 and 1.07 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.26 (*s*, CH_3O); 3.68 (*d*×*d*, *J*=8, *J'*=3, 1 H–C(19)); 3.80 (*m*, H–C(17)); 3.86 (*d*, *J*=8, 1 H–C(19)); 5.53 (*d*×*d*, *J*=6, *J'*=2, H–C(6)). – MS.: *346* (M^+, 100), 328 (24), 313 (20), 303 (47), 285 (40).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androst-5-en-17α-ol (**7**). M.p. 151–152°, $[\alpha]_D = -71°$ (*c*=0.70). – IR.: 3615, 1380, 1330, 1130, 1086, 1062, 1040, 1015, 975, 945, 916, 910, 885. – ^{1}H-NMR.: 0.88, 1.08 and 1.10 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.32 (*s*, CH_3O); 3.65 (*d*×*d*, *J*=8, *J'*=3, 1 H–C(19)); 3.89 (*d*, *J*=8, 1 H–C(19)); 5.55 (*d*×*d*, *J*=6, *J'*=2, H–C(6)). – MS.: *346* (M^+, 100), 303 (87), 285 (24), 271 (24), 259 (32).

3β,19:8β,17β-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-7α-ol (**8**) was isolated after treatment of **56** (s. below) with methanol/K_2CO_3 and water. M.p. 245°, $[\alpha]_D = -30°$ (*c*=0.50). – IR.: 3620, 1460, 1438, 1382, 1360, 1335, 1148, 1125, 1095, 1050, 1035, 1000, 975, 960, 903, 890, 875. – ^{1}H-NMR.: 0.90 and 0.98 (2*s*, 6 H and 3 H, resp., 2 H_3C–C(4) and H_3C(18)); 3.20 (*s*, CH_3O); 3.71 (*d*×*d*, *J*=10, *J'*=2, 1 H–C(19)); 3.77 (*m*, H–C(17)); 3.98 (*t*, *J*=4, H–C(7)); 4.13 (*d*×*d*, *J*=10, *J'*=3, 1 H–C(19)). – MS.: *362* (M^+, 100), 344 (18), 301 (13), 275 (13), 257 (15).

$C_{22}H_{34}O_4$ (362.49) Calc. C 72.86 H 9.45% Found C 72.86 H 9.34%

3β,19:8β,17β-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-7α-ol acetate (**9**). M.p. 185–187°. – IR.: 1725, 1460, 1440, 1370, 1335, 1250, 1152, 1130, 1100, 1082, 1040, 1005, 978, 965, 943, 905, 865. – ^{1}H-NMR.: 0.88, 0.89 and 0.92 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.03 (*s*, CH_3COO); 3.20 (*s*, CH_3O); 3.73 (*d*×*d*, *J*=10, *J'*=1.5, 1 H–C(19)); 3.78 (*m*, $w_{1/2}$=3, H–C(17)); 4.13 (*d*×*d*, *J*=10, *J'*=3, 1 H–C(19)); 5.03 (*t*, *J*=3, H–C(7)). – MS.: 404 (M^+, 48), 388 (11), 362 (20), *344* (100), 301 (44), 257 (32), 43 (53).

3β,19:8β,17β-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-7-one (**10**) was obtained by *Jones* oxidation of **8**. M.p. 244–246°. – IR.: 1710, 1135, 1110, 1090, 1038, 998, 975, 905, 870. – ^{1}H-NMR.: 0.92, 0.94 and 0.98 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.21 (*s*, CH_3O); 3.61 (*d*×*d*, *J*=10, *J'*=2, 1 H–C(19)); 3.88 (*m*, $w_{1/2}$=3, H–C(17)); 3.97 (*d*×*d*, *J*=10, *J'*=3, 1 H–C(19)). – MS.: *360* (M^+, 100), 330 (22), 273 (42), 263 (25), 231 (33).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androst-5-en-17β-ol acetate (**11**). M.p. 108–110°, $[\alpha]_D = -45°$ (*c*=1.65). – IR.: 1720, 1455, 1375, 1360, 1330, 1250, 1130, 1098, 1085, 1040, 1015, 985, 975, 952, 940, 918, 900. – ^{1}H-NMR.: 0.88, 1.06 and 1.09 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.96 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.69 (*d*×*d*, *J*=8, *J'*=3, 1 H–C(19)); 3.90 (*d*, *J*=8, 1 H–C(19)); 4.82 (*m*, H–C(17)); 5.56 (*m*, H–C(6)). – MS.: 388 (M^+, 71), 345 (46), 328 (96), 313 (46), *285* (100), 241 (88), 201 (62), 105 (58), 91 (60), 43 (91).

General procedure for the preparation of the ring-B-dienes **12**, **31** *(Scheme 3),* **19** *(Scheme 5),* **50** *and* **51** *(Scheme 6).* 1,3-Dibromo-5,5-dimethylhydantoine (125 mg) was added to a refluxing solution of the Δ^5-compound (620 mg) in 27 ml of benzene/hexane 5:4. After 20 min boiling the mixture

was cooled and filtered; dimethylformamide (4 ml), LiBr (*ca.* 50 mg) and Li_2CO_3 (*ca.* 50 mg) were added to the filtrate. The mixture was heated to 140° for 15 min with simultaneous stripping of benzene/hexane. After normal work-up and recrystallization the $\Delta^{5,7}$-diene was obtained in about 60% yield[26])[27]).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androsta-5,7-dien-17β-ol acetate (**12**). M.p. 112°, $[\alpha]_D = +400°$ ($c = 0.58$). – UV.: 265 sh (7340), 274 (10,320), 285 (10,800), 297 (6370). – IR.: 1720, 1660, 1375, 1325, 1250, 1132, 1088, 1045, 1020, 945, 900, 845. – ^{1}H-NMR.: 0.99, 1.10 and 1.14 (3*s*, $2\,H_3C$–C(4) and H_3C(18)); 1.92 (*s*, CH_3COO)); 3.27 (*s*, CH_3O); 3.74 (*d*, $J = 8$, 1 H–C(19)); 4.03 (*d*×*d*, $J = 8$, $J' = 2$, 1 H–C(19)); 4.71 (*m*, H–C(17)); 5.52 (br. *d*, $J = 6$, H–C(7)); 5.68 (*d*, $J = 6$, H–C(6)). – MS.: 386 (M^+, 9), 343 (5), 326 (20), 311 (11), 299 (50), 283 (26), 239 (63), *43* (100), 18 (37).

$C_{24}H_{34}O_4$ (386.51) Calc. C 74.57 H 8.87% Found C 74.40 H 8.83%

General procedure for hydrogenation. a) *With 5% Pd/C:* about 100 mg of reactant were dissolved in 10 ml of pure alcohol and hydrogenated at RT. with 20% Pd/C (check by TLC.).

b) *With* Raney-*nickel:* the ring B dienes were dissolved in pure dioxane (about 100 mg of reactant in 10 ml of solvent). After addition of the same amount of *Raney*-nickel[28]) the dienes were hydrogenated for 4 h at RT. The crude mixture was separated by chromatography on silicagel (benzene/ethyl acetate 19:1).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-7-en-17β-ol acetate (**13**). M.p. 94–96°, $[\alpha]_D = -12°$ ($c = 0.68$). – IR.: 1718, 1465, 1455, 1435, 1370, 1360, 1328, 1312, 1248, 1157, 1130, 1108, 1078, 1030, 989, 965, 947, 895. – ^{1}H-NMR.: 0.94, 0.96 and 1.01 (3*s*, $2\,H_3C$–C(4) and H_3C(18)); 1.93 (*s*, CH_3COO); 3.22 (*s*, CH_3O); 3.70 (*d*×*d*, $J = 9$, $J' = 1.5$, 1 H–C(19)); 3.86 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.72 (*m*, H–C(17)); 5.51 (*m*, H–C(7)). – MS.: 388 (M^+, 32), 345 (13), 328 (61), 285 (76), 280 (61), 241 (71), 185 (95), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9.34% Found C 73.94 H 9.28%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-17β-ol acetate (**14**). M.p. 152°, $[\alpha]_D = +2°$ ($c = 1.85$). – IR.: 1715, 1455, 1372, 1335, 1250, 1145, 1122, 1100, 1072, 1038, 995, 968, 900, 878. – ^{1}H-NMR.: 0.90 and 1.00 (2*s*, 6 H and 3 H, resp., $2\,H_3C$–C(4) and H_3C(18)); 1.98 (*s*, CH_3COO); 3.23 (*s*, CH_3O); 3.77 (br. *d*, $J = 8$, 1 H–C(19)); 3.94 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 4.90 (*d*, $J = 4$, H–C(17)). – MS.: 388 (M^+, 29), 345 (15), 328 (65), 285 (32), 259 (32), 241 (38), 185 (54), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9.34% Found C 74.08 H 9.35%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-17β-ol acetate (**15**). M.p. 147°, $[\alpha]_D = +43°$ ($c = 0.67$). – IR.: 1720, 1465, 1372, 1361, 1329, 1290, 1250, 1140, 1120, 1105, 1092, 1041, 1015, 952, 930, 905. – ^{1}H-NMR.: 0.88 and 0.97 (2*s*, 3 H and 6 H, resp., $2\,H_3C$–C(4) and H_3C(18)); 2.01 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.84 (*d*×*d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.98 (br. *d*, $J = 9$, 1 H–C(19)); 4.81 (*m*, H–C(17)). – MS.: 388 (M^+, 57), 360 (7), 345 (22), 328 (65), 285 (48), 241 (50), 185 (77), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9,34% Found C 74.05 H 9.29%

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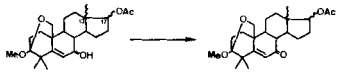
[26]) HBr-*elimination* with triethyl phosphite in xylene [8] gave the same yield.

[27]) In about 5% yield the allylic alcohols **xi**, **xii**, and **xiii**, respectively, were obtained. They were the main product when the corresponding crude bromination product was chromatographed on wet silicagel. *Jones* oxidation of the allylic alcohols afforded the corresponding enones **xiv**, **xv**, and **xvi**, respectively. For analytical data see [11].



xi 13α,17β
xii 13α,17α
xiii 13β,17β

xiv 13α,17β
xv 13α,17α
xvi 13β,17β

[28]) Nickel-aluminium alloy (400 mg) in water (12 ml) was treated portionwise with solide NaOH (1.5 g). After warming to 70° for 1 h the water was decanted and the catalyst washed five times with water (10 ml) and four times with dioxane (10 ml).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,8α,13α-androst-6-en-17β-ol acetate (**16**). M.p. 108–110°, $[\alpha]_D = +91°$ ($c = 1.80$). – IR.: 1722, 1468, 1385, 1375, 1365, 1325, 1255, 1160, 1110, 1092, 1072, 1030, 975, 900. – ^{1}H-NMR.: 1.00, 1.01 and 1.03 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.00 (*s*, CH_3COO); 3.25 (*s*, CH_3O); 3.77 (*d*×*d*, $J = 8$, $J' = 2$, 1 H–C(19)); 4.03 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 4.86 (*m*, H–C(17)); 5.44–5.80 (*m*, H–C(6) and H–C(7)). – MS.: 388 (M^+, 14), 328 (54), 285 (40), 241 (57), 240 (57), 185 (83), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,8α,13α-androstan-17β-ol acetate (**17**). M.p. 129–131°, $[\alpha]_D = +113°$ ($c = 0.425$). – IR.: 1722, 1465, 1382, 1375, 1365, 1330, 1255, 1155, 1110, 1090, 1070, 1038, 942, 900. – ^{1}H-NMR.: 0.92, 0.94 and 0.97 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.00 (*s*, CH_3COO); 3.24 (*s*, CH_3O); 3.80 (br. *d*, $J = 8$, 1 H–C(19)); 4.22 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 4.74 (*m*, H–C(17)). – MS.: 390 (M^+, 6), 330 (74), 274 (97), 187 (49), 133 (77), 82 (62), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androst-5-en-17α-ol acetate (**18**). M.p. 112–114°, $[\alpha]_D = -80°$ (1.20). – IR.: 1732, 1380, 1330, 1305, 1250, 1130, 1100, 1090, 1065, 1040, 1018, 975, 945, 915, 905, 895. – ^{1}H-NMR.: 0.90, 1.04 and 1.06 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.98 (*s*, CH_3COO); 3.24 (*s*, CH_3O); 3.66 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 3.84 (*d*, $J = 8$, 1 H–C(19)); 5.07 (*t*, $J = 8$, H–C(17)); 5.51 (*d*×*d*, $J = 6$, $J' = 2$, H–C(6)). – MS.: 388 (M^+, 27), 345 (42), 328 (25), 285 (41), 241 (26), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-13α-androsta-5,7-dien-17α-ol acetate (**19**). M.p. 115°, $[\alpha]_D = +533°$ ($c = 0.555$). – UV.: 265 (8080), 273 (11,420), 283 (12,045), 296 (6960). – IR.: 1720, 1465, 1453, 1380, 1375, 1360, 1325, 1295, 1250, 1130, 1088, 1045, 1010, 942, 902, 888, 840, 828. – ^{1}H-NMR.: 0.98, 1.08 and 1.15 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.97 (*s*, CH_3COO); 3.27 (*s*, CH_3O); 3.75 (*d*, $J = 8$, 1 H–C(19)); 4.11 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 4.88 (*t*, $J = 8$, H–C(17)); 5.49 (*d*×*d*, $J = 6$, $J' = 2$, H–C(7)); 5.64 (*d*, $J = 6$, H–C(6)). – MS.: 386 (M^+, 16), 343 (9), 326 (25), 311 (19), *299* (100), 283 (41), 239 (63), 43 (82).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-7-en-17α-ol acetate (**20**). M.p. 143°, $[\alpha]_D = -43°$ ($c = 1.50$). – IR.: 1725, 1385, 1375, 1363, 1335, 1318, 1308, 1255, 1165, 1135, 1105, 1085, 1065, 1045, 1033, 990, 970, 945, 898. – ^{1}H-NMR.: 0.94, 0.96 and 1.00 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.98 (*s*, CH_3COO); 3.23 (*s*, CH_3O); 3.67 (*d*×*d*, $J = 9$, $J' = 1$, 1 H–C(19)); 3.85 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.81 (*t*, $J = 7$, H–C(17)); 5.56 (*m*, H–C(7)). – MS.: 388 (M^+, 52), 345 (16), 328 (78), 285 (61), 241 (55), 185 (71), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9.34% Found C 74.49 H 9.44%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-17α-ol acetate (**21**). M.p. 119–121°, $[\alpha]_D = +96°$ ($c = 3.07$). – IR.: 1720, 1468, 1445, 1380, 1375, 1365, 1335, 1305, 1255, 1158, 1145, 1115, 1095, 1072, 1048, 1038, 982, 970, 940, 910, 850. – ^{1}H-NMR.: 0.81, 0.96 and 0.97 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.02 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.74–4.00 (*m*, $w_{1/2} = 6$, 2 H–C(19)); 4.78 (*m*, H–C(17)). – MS.: (M^+, 90), 345 (23), 332 (47), 328 (83), 285 (73), 241 (60), 185 (96), *43* (100).

17β,19-Diacetoxy-4,4-dimethyl-13α-androsta-5,7-dien-3-one (**22**). M.p. 104–106°, $[\alpha]_D = +18°$ ($c = 2.32$). – UV.: 239 sh (1616), 244 sh (2220), 249 sh (3230), 255 sh (4443), 261 sh (5350), 280 (7674). – IR.: 1728, 1715, 1460, 1410, 1380, 1365, 1250, 1140, 1120, 1048, 1032, 977, 920, 835. – ^{1}H-NMR.: 1.02, 1.30 and 1.32 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.93 and 2.04 (2*s*, 2 CH_3COO); 3.98 and 4.14 (2*d*, $J = 11$, 2 H–C(19)); 4.82 (*m*, H–C(17)); 5.75 (*m*, H–C(7)); 5.97 (*d*, $J = 6$, H–C(6)). – MS.: 414 (M^+, 19), *281* (100), 225 (16), 197 (16), 43 (19).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-13α-androsta-5,7-dien-3-one (**23**). M.p. 115°, $[\alpha]_D = +157°$ ($c = 2.25$). – UV.: 265 sh (6434), 277 (8720), 285 (9230), 295 sh (6690). – IR.: 3620, 3585, 1715, 1460, 1410, 1378, 1362, 1255, 1128, 1050, 990, 978, 945, 835. – ^{1}H-NMR. ($CDCl_3/D_2O$)[29]: 1.01, 1.28 and 1.32 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 3.03 (*s*, CH_3COO); 3.56 (*m*, $w_{1/2} = 3$, 2 H–C(19)); 4.80 (*m*, H–C(17)); 5.69 (*m*, H–C(7)); 5.99 (*d*, $J = 6$, H–C(6)). – MS.: 372 (M^+, 10), 342 (26), 282 (70), *281* (100), 239 (32), 225 (49), 197 (49), 43 (39).

$C_{23}H_{32}O_4$ (372.49) Calc. C 74.16 H 8.66% Found C 74.01 H 8.65%

17β,19-Diacetoxy-4,4-dimethyl-5α,13α-androst-7-en-3-one (**24**). M.p. 79–81°, $[\alpha]_D = -46°$ ($c = 2.10$). – IR.: 1728, 1710, 1455, 1377, 1250, 1130, 1040, 995, 910, 845. – ^{1}H-NMR.: 1.02, 1.10

[29]) The spectrum measured in pure $CDCl_3$ shows broad signals due to the equilibrium of the hydroxyketone and the corresponding hemiacetal (s. also footnote 25).

and 1.14 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.00 and 2.02 (2*s*, 2 CH_3COO); 4.22 and 4.53 (2*d*, *J* = 12, 2 H–C(19)); 4.74 (br. *t*, *J* = 6, H–C(17)); 5.52 (*m*, H–C(7)). – MS.: 416 (M^+, 4), 356 (56), 341 (21), 315 (15), 296 (68), 283 (39), 265 (27), 197 (44), *43* (100).

17β,19-Diacetoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-3-one (**25**). M.p. 124–126°, $[\alpha]_D = +12°$ (*c* = 0.985). – IR.: 1725, 1710 sh, 1455, 1375, 1305, 1250, 1160, 1145, 1130, 1075, 1045, 1025, 995, 970, 940, 920, 890, 872, 838. – ^{1}H-NMR.: 0.94, 1.06 and 1.14 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.97 and 1.98 (2*s*, 2 CH_3COO); 4.04 and 4.33 (2 *d*, *J* = 12, 2 H–C(19)); 4.91 (br. *d*, *J* = 3, H–C(17)). – MS.: 416 (M^+, 9), *356* (100), 296 (59), 283 (45), 265 (23), 43 (82).

17β,19-Diacetoxy-4,4-dimethyl-5α,13α-androst-8-en-3-one (**26**). M.p. 129–131°, $[\alpha]_D = +88°$ (*c* = 1.05). – IR.: 1725, 1710 sh, 1460, 1383, 1368, 1250, 1190, 1108, 1055, 1038, 980, 870. – ^{1}H-NMR.: 0.92, 1.06 and 1.11 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.96 and 2.01 (2*s*, 2 CH_3COO); 3.96 and 4.36 (2*d*, *J* = 12, 2 H–C(19)); 5.82 (br. *t*, *J* = 6, H–C(17)). – MS.: 416 (M^+, 2), 356 (26), 343 (22), 296 (41), *283* (100), 43 (59).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α,13α-androst-7-en-3-one (**27**). M.p. 153–155°, $[\alpha]_D = -33°$ (*c* = 2.40). – IR.: 3590, 1720, 1470, 1440, 1378, 1365, 1320, 1255, 1160, 1120, 1039, 989, 948, 900. – ^{1}H-NMR.: 0.98, 0.99 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.95 (*s*, CH_3COO); 3.66–4.04 (*m*, $w_{1/2}$ = 6, 2 H–C(19)); 4.73 (*m*, H–C(17)); 5.51 (*m*, H–C(7)). – MS.: 374 (M^+, 50), *314* (100), 283 (71), 271 (54), 241 (50), 43 (64).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α,13α-androst-8(14)-en-3-one (**28**). M.p. 121–123°, $[\alpha]_D = -16°$ (*c* = 1.2). – IR.: 3590, 1720, 1468, 1445, 1375, 1250, 1160, 1142, 1115, 1065, 1050, 1030, 995, 968, 900, 879. – ^{1}H-NMR.: 0.91, 0.94 and 1.04 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.98 (*s*, CH_3COO); 3.70–4.00 (*m*, $w_{1/2}$ = 5, 2 H–C(19)); 4.90 (br. *d*, *J* = 3, H–C(17)). – MS.: 374 (M^+, 55), *314* (100), 299 (20), 296 (27), 283 (35), 265 (41), 43 (37).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α,13α-androst-8-en-3-one (**29**). M.p. 167°, $[\alpha]_D = +80°$ (*c* = 2.15). – IR.: 3590, 1720, 1468, 1375, 1365, 1290, 1250, 1135, 1095, 1085, 1060, 1045, 1018, 980, 955, 930, 910. – ^{1}H-NMR.: 0.88, 0.97 and 1.02 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.01 (*s*, CH_3COO); 3.82 (*d*×*d*, *J* = 9, *J'* = 3, 1 H–C(19)); 3.96 (br. *d*, *J* = 9, 1 H–C(19)); 4.80 (br. *t*, *J* = 8, H–C(17)). – MS.: 374 (M^+, 44), 344 (53), 314 (58), 283 (98), 241 (51), *43* (100).

$C_{23}H_{34}O_4$ (374.50) Calc. C 73.76 H 9.15% Found C 73.62 H 9.12%

3β,19-Epoxy-3α-methoxy-4,4-dimethylandrost-5-en-17β-ol acetate (**30**). M.p. 160–162°, $[\alpha]_D = -56°$ (*c* = 1.10). – IR.: 1720, 1464, 1460, 1373, 1356, 1338, 1288, 1250, 1145, 1135, 1085, 1025, 993, 970, 955, 920, 900, 860, 840. – ^{1}H-NMR.: 0.76 (*s*, H_3C(18)); 1.05 and 1.08 (2*s*, 2 H_3C–C(4)); 2.00 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.70 (*d*×*d*, *J* = 8, *J'* = 3, 1 H–C(19)); 3.94 (*d*, *J* = 8, 1 H–C(19)); 5.57 (*d*×*d*, *J* = 8, *J'* = 6, H–C(17)); 5.53 (*d*×*d*, *J* = 6, *J'* = 2, H–C(6)). – MS.: 388 (M^+, 39), 345 (21), 328 (12), 285 (14), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethylandrosta-5,7-dien-17β-ol acetate (**31**). M.p. 139°, $[\alpha]_D = +215°$ (*c* = 1.00). – UV.: 265 sh (12,695), 274 (16,160), 285 (15,770), 296 (9230). – IR.: 1725, 1668, 1615, 1469, 1455, 1449, 1380, 1375, 1360, 1330, 1250, 1175, 1133, 1090, 1069, 1032, 995, 980, 942, 910, 902, 870, 845. – ^{1}H-NMR.: 0.66 (*s*, H_3C(18)); 1.08 and 1.14 (2*s*, 2 H_3C–C(4)); 2.00 (*s*, CH_3COO); 2.27 (*s*, CH_3O); 3.84 (*d*, *J* = 8, 1 H–C(19)); 3.97 (*d*×*d*, *J* = 8, *J'* = 2, 1 H–C(19)); 4.68 (*m*, H–C(17)); 5.41 (br. *d*, *J* = 6, H–C(7)); 5.67 (*d*, *J* = 6, H–C(6)). – MS.: 386 (M^+, 34), 371 (6), 343 (24), 311 (22), *299* (100), 283 (44), 251 (30), 43 (54).

$C_{24}H_{34}O_4$ (386.51) Calc. C 74.57 H 8.87% Found C 74.45 H 8.92%

17β,19-Diacetoxy-4,4-dimethylandrosta-5,7-dien-3-one (**32**). M.p. 132°, $[\alpha]_D = -123°$ (*c* = 4.80). – UV.: 265 sh (7870), 273 (9910), 282 (950), 294 sh (5360). – IR.: 1728, 1712, 1650, 1460, 1411, 1388, 1375, 1363, 1330, 1250, 1158, 1137, 1112, 1088, 1064, 1042, 1032, 976, 910, 845. – ^{1}H-NMR.: 0.72 (*s*, H_3C(18)); 1.28 and 1.32 (2*s*, 2 H_3C–C(4)); 1.90 and 2.02 (2*s*, 2 CH_3COO); 4.10 and 4.23 (2*d*, *J* = 11, 2 H–C(19)); 4.62–4.80 (*m*, H–C(17)); 5.59 (*m*, H–C(7)); 5.94 (*d*, *J* = 8, H–C(6)). – MS.: 414 (M^+, 16), 354 (3), *341* (100), 299 (11), 285 (45), 281 (24), 257 (59), 71 (23), 43 (54).

$C_{25}H_{34}O_5$ (414.52) Calc. C 72.43 H 8.27% Found C 72.47 H 8.33%

17β-Acetoxy-19-hydroxy-4,4-dimethylandrosta-5,7-dien-3-one (**33**). M.p. 198°, $[\alpha]_D = +128°$ (*c* = 1.50). – UV.: 265 sh (6827), 274 (9103), 286 (9234), 296 (5602). – IR.: 3590, 1721, 1460 br.,

1385, 1373, 1360, 1255, 1120 br., 1048, 1030, 940, 912 br., 870, 848. – ^{1}H-NMR. ($CDCl_3/D_2O$)[30]: 0.66 and 0.76 (2*s*, 3 H, $H_3C(18)$); 1.14, 1.17, 1.30 and 1.32 (4*s*, 6 H, 2 H_3C–C(4)); 2.01 and 2.03 (2*s*, 3 H, CH_3COO); 3.52 and 3.70 (2*d*, J = 11, 1 H, H–C(19)); 3.92 (*m*, $w_{1/2}$ = 3, 1 H, H–C(19)); 4.60–4.82 (*m*, 1 H, H–C(17)); 5.36–5.56 (*m*, 1 H, H–C(7)); 5.69 (*d*, J = 6, ½ H, H–C(6)); 6.02 (*d*, J = 6, ½ H, H–C(6)). – MS.: 372 (M^+, 38), *341* (100), 324 (20), 299 (35), 285 (65), 281 (28), 257 (94), 43 (81).

$C_{23}H_{32}O_4$ (372.49) Calc. C 74.16 H 8.66% Found C 74.14 H 8.58%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-7-en-17β-ol acetate (**34**). M.p. 173–175°, $[\alpha]_D$ = +12° (c = 0.515). – IR.: 1720, 1465, 1455, 1445, 1435, 1381, 1370, 1359, 1329, 1250, 1161, 1146, 1119, 1100, 1082, 1075, 1025, 990, 975, 965, 906, 895, 857, 841, 828. – ^{1}H-NMR.: 0.59 ($H_3C(18)$); 0.95 and 1.05 (2*s*, 2 H_3C–C(4)); 2.00 (CH_3COO); 3.23 (*s*, CH_3O); 3.7–3.9 (*m*, $w_{1/2}$ = 5, 2 H–C(19)); 4.69 (*m*, H–C(17)); 5.28 (*m*, H–C(7)). – MS.: 388 (M^+, 53), 345 (24), 328 (51), 313 (40), 301 (33), 285 (40), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9.34% Found C 74.15 H 9.30%

17β,19-Diacetoxy-4,4-dimethyl-5α-androst-7-en-3-one (**35**). M.p. 107–109°, $[\alpha]_D$ = −52° (c = 2.55). – IR.: 1725, 1710 sh, 1390, 1375, 1250, 1155, 1130, 1100, 1082, 1032 br., 985, 910, 855. – ^{1}H-NMR.: 0.67 (*s*, $H_3C(18)$); 1.10 and 1.17 (2*s*, 2 H_3C–C(4)); 2.01 and 2.04 (2*s*, 2 CH_3COO); 4.23 and 4.52 (2*d*, J = 13, 2 H–C(19)); 4.69 (*m*, H–C(17)); 5.23 (*m*, H–C(7)). – MS.: 416 (M^+, 4), 356 (29), 325 (96), 270 (56), 257 (73), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8(14)-en-17β-ol acetate (**36**). M.p. 150°, $[\alpha]_D$ = −13° (c = 0.790). – IR.: 1722, 1460, 1435, 1370, 1358, 1328, 1288, 1248, 1145, 1120, 1088, 1030, 990, 970, 915, 895, 870. – ^{1}H-NMR.: 0.85 (*s*, $H_3C(18)$); 0.91 and 1.00 (2*s*, 2 H_3C–C(4)); 2.01 (*s*, CH_3COO); 3.22 (*s*, CH_3O); 3.75 (*d*×*d*, J = 9, J' = 3, 1 H–C(19)); 3.88 (br. *d*, J = 9, 1 H–C(19)); 4.54 (*d*×*d*, J = 10, J' = 6, H–C(17)). – MS.: 388 (M^+, 80), 345 (22), 328 (81), 313 (30), 301 (31), 285 (31), 272 (22), 259 (30), 241 (41), 185 (46), *43* (100).

$C_{24}H_{36}O_4$ (388.53) Calc. C 74.19 H 9.34% Found C 74.30 H 9.46%

17β,19-Diacetoxy-4,4-dimethyl-5α-androst-8(14)-en-3-one (**37**). M.p. 103–105°, $[\alpha]_D$ = −28° (c = 2.00). – IR.: 1730, 1705, 1465, 1436, 1390, 1375, 1335, 1295, 1250, 1155, 1140, 1065, 1040, 1010, 993, 980, 970, 950, 918, 867. – ^{1}H-NMR.: 0.92 and 1.11 (2*s*, 3 H and 6 H, resp., 2 H_3C–C(4) and $H_3C(18)$); 2.04 (*s*, 6 H, 2 CH_3COO); 4.07 and 4.46 (2*d*, J = 12, 2 H–C(19)); 4.56 (*d*×*d*, J = 10, J' = 7, H–C(17)). – MS.: 416 (M^+, 20), 398 (5), 356 (39), 325 (30), 313 (14), 296 (42), 283 (71), *43* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8-en-17β-ol acetate (**38**). M.p. 206–208°, $[\alpha]_D$ = +128° (c = 2.40). – IR.: 1722, 1470, 1448, 1436, 1388, 1375, 1365, 1332, 1285, 1260, 1143, 1120, 1110, 1085, 1078, 1048, 1030, 990, 978, 948, 905, 862, 849. – ^{1}H-NMR.: 0.69 (*s*, $H_3C(18)$); 0.97 (*s*, 6 H, 2 H_3C–C(4)); 2.01 (*s*, CH_3COO); 3.27 (*s*, CH_3O); 3.83 (*d*×*d*, J = 10, J' = 2, 1 H–C(19)); 3.95 (br. *d*, J = 10, 1 H–C(19)); 4.65 (*d*×*d*, J = 9, J' = 6, H–C(17)). – MS.: 388 (M^+, 58), 345 (30), 328 (55), 313 (36), 301 (26), 285 (28), 259 (40), *43* (100).

17β,19-Diacetoxy-4,4-dimethyl-5α-androst-8-en-3-one (**39**). M.p. 73–75°, $[\alpha]_D$ = +96° (c = 3.10). – IR.: 1725, 1710 sh, 1461, 1430 br., 1386, 1372, 1250, 1140 br., 1110 br., 1080 br., 1045 sh, 1030, 980, 945. – ^{1}H-NMR.: 0.73 (*s*, $H_3C(18)$); 1.04 and 1.10 (2*s*, 2 H_3C–C(4)); 1.99 and 2.02 (2*s*, 2 CH_3COO); 4.02 and 4.34 (2*d*, J = 11, 2 H–C(19)); 4.56–4.76 (*m*, H–C(17)). – MS.: 416 (M^+, 1), 356 (36), 343 (14), 313 (40), *283* (100), 43 (82).

3β,19:8α,14α-Diepoxy-3α-methoxy-4,4-dimethyl-5α-androstan-17β-ol acetate (**40**). M.p. 175°, $[\alpha]_D$ = +91° (c = 1.05). – IR.: 1730, 1470, 1460, 1440, 1385, 1375, 1362, 1347, 1295, 1250, 1150, 1140, 1125, 1098, 1040, 1022, 980, 945, 922, 900, 884. – ^{1}H-NMR.: 0.93, 0.96 and 1.00 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.03 (*s*, CH_3COO); 3.22 (*s*, CH_3O); 3.72 (*d*×*d*, J = 9, J' = 1, 1 H–C(19)); 4.19 (*d*×*d*, J = 9, J' = 3, 1 H–C(19)); 4.78 (*m*, H–C(17)). – MS.: 404 (M^+, 86), 389 (5), 386 (6), 348 (23), 317 (22), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.51 H 9.21%

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[30] The NMR. spectrum shows two substances, obviously the hydroxyketone and the corresponding hemiacetal.

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androsta-8,14-dien-17β-ol (**41**). M.p. 171–173°, $[\alpha]_D = +175°$ ($c = 1.35$). – UV.: 246 sh (21,465), 252 (22,566), 260 sh (16,510). – IR.: 3610, 1465, 1388, 1365, 1332, 1145, 1120, 1105, 1088, 1073, 1043, 1029, 999, 978, 965, 935, 912, 905, 873, 860. – ^{1}H-NMR.: 0.87, 0.97 and 0.98 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.27 (*s*, CH_3COO); 3.82–3.94 (*m*, $w_{1/2} = 3$, 2 H–C(19)); 3.97 (br. *t*, $J = 8$, H–C(17)); 5.28 (br. *t*, $J = 3$, H–C(15)). – MS.: *344* (M^+, 100), 314 (12), 301 (23), 288 (35), 258 (37), 216 (30), 43 (35).

$C_{22}H_{32}O_3$ (344.48) Calc. C 76.70 H 9.36% Found C 76.97 H 9.48%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8-en-17β-ol (**42**). M.p. 164°, $[\alpha] = +162°$ ($c = 5.25$). – IR.: 3610, 1470, 1388, 1378, 1365, 1332, 1145, 1120, 1110, 1082, 1045, 1024, 1000, 990, 972, 965, 945, 921, 902, 858. – ^{1}H-NMR.: 0.64 (*s*, H_3C(18)); 0.96 (*s*, 6 H, 2 H_3C–C(4)); 3.26 (*s*, CH_3O); 3.68 (*m*, H–C(17)); 3.83 (*d*×*d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.94 (br. *d*, $J = 9$, 1 H–C(19)). – MS.: *346* (M^+, 100), 303 (35), 290 (23), 271 (13), 259 (25).

$C_{22}H_{34}O_3$ (346.49) Calc. C 76.26 H 9.89% Found C 75.93 H 9.95%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8(14)-en-17β-ol (**43**). M.p. 132°, $[\alpha]_D = +27°$ ($c = 1.85$). – IR.: 3610, 1470, 1460, 1438, 1385, 1362, 1332, 1145, 1122, 1090, 1070, 1038, 972, 922, 900, 872. – ^{1}H-NMR.: 0.81, 0.92 and 1.01 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.23 (*s*, CH_3O); 3.51 (*m*, H–C(17)); 3.68–3.96 (*m*, $w_{1/2} = 7$, 2 H–C(19)). – MS.: *346* (M^+, 100), 303 (31), 290 (23), 259 (41), 185 (22).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α-androst-8-en-3-one (**44**). M.p. 143°, $[\alpha]_D = +114°$ ($c = 4.15$). – IR.: 3590, 1722, 1468, 1445, 1388, 1375, 1315, 1285, 1255, 1159, 1146, 1104, 1085, 1065, 1030, 945, 906, 860. – ^{1}H-NMR.: 0.68 (*s*, H_3C(18)); 0.97 and 1.03 (2*s*, 2 H_3C–C(4)); 2.01 (*s*, CH_3COO); 3.81 (*d*×*d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.94 (*d*, $J = 9$, 1 H–C(19)); 4.63 (*d*×*d*, $J = 9$, $J' = 6$, H–C(17)). – MS.: 374 (M^+, 35), 343 (38), 331 (17), 314 (34), 301 (19), 299 (20), *283* (100), 271 (27), 43 (59).

$C_{23}H_{34}O_4$ (374.50) Calc. C 73.76 H 9.15% Found C 73.74 H 9.23%

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α-androst-7-en-3-one (**45**). M.p. 171°, $[\alpha]_D = -18°$ ($c = 2.95$). – IR.: 3590, 1725, 1469, 1449, 1388, 1375, 1362, 1320, 1255, 1168, 1150, 1115, 1099, 1068, 1030, 990, 978, 975, 938, 911, 900, 860, 845. – ^{1}H-NMR.: 0.59 (*s*, H_3C(18)); 1.00 and 1.05 (2*s*, 2 H_3C–C(4)); 2.00 (*s*, CH_3COO); 3.83 (*m*, $w_{1/2} = 4$, 2 H–C(19)); 4.67 (*m*, H–C(17)); 5.26 (*m*, H–C(7)). – MS.: 374 (M^+, 72), 356 (8), 331 (19), 325 (31), 318 (33), 314 (47), 271 (44), 257 (64), *43* (100).

$C_{23}H_{34}O_4$ (374.50) Calc. C 73.76 H 9.15% Found C 73.70 H 9.22%

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α-androst-8(14)-en-3-one (**46**). M.p. 125–127°, $[\alpha]_D = -24°$ ($c = 1.65$). – IR.: 3590, 1725, 1468, 1440, 1372, 1360, 1320, 1292, 1250, 1170, 1145, 1110, 1090, 1063, 1038, 992, 968, 900, 872. – ^{1}H-NMR.: 0.86, 0.94 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.02 (*s*, CH_3COO); 3.76 (*d*×*d*, $J = 8$, $J' = 3$, 1 H–C(19)); 3.91 (br. *d*, $J = 8$, 1 H–C(19)); 4.53 (*d*×*d*, $J = 11$, $J' = 7$, H–C(17)). – MS.: 374 (M^+, 98), 331 (23), *314* (100), 301 (33), 299 (35), 283 (60), 43 (63).

$C_{23}H_{34}O_4$ (374.50) Calc. C 73.76 H 9.15% Found C 73.62 H 9.24%

4,4-Dimethyl-13α-androst-5-ene (**48**). M.p. 44–47°, $[\alpha]_D = -150°$ ($c = 2.05$). – IR.: 1460, 1450, 1383, 1375, 1361. – ^{1}H-NMR.: 0.86, 0.98, 1.04 and 1.09 (4*s*, H_3C(18), H_3C(19) and 2 H_3C–C(4)); 2.26–2.48 (*m*, 1 H–C(7)); 5.46 (*t*, $J = 3$, H–C(6)). – MS.: 286 (M^+, 72), 271 (100).

4,4-Dimethyl-13α-androsta-5,7-diene (**50**). $[\alpha]_D = -33°$ ($c = 2.40$). – UV.: 277 (5300). – IR. (CCl_4): 3030, 1450, 1368, 1285, 1185, 1155, 1145, 1075, 990, 980, 909, 825. – ^{1}H-NMR.: 0.83, 0.97, 1.09 and 1.12 (4*s*, H_3C(18), H_3C(19) and 2 H_3C–C(4)); 5.63 (*m*, H–C(7)); 5.84 (*d*, $J = 6$, H–C(6)). – MS.: 284 (M^+, 62), 269 (76), 213 (46), 199 (97), *173* (100).

4,4-Dimethyl-5α,13α-androst-8-ene (**53**). $[\alpha]_D = +8°$ ($c = 3.05$). – IR. (CCl_4): 1455, 1370, 1328, 1275, 1235, 1205, 1164, 1138, 1035, 972, 945, 928. – ^{1}H-NMR.: 0.82, 0.86, 0.87 and 0.92 (4*s*, H_3C(18), H_3C(19) and 2 H_3C–C(4)). – MS.: 286 (M^+, 28), *271* (100), 201 (22), 189 (11), 175 (40).

4,4-Dimethyl-5α-androst-7-ene (**54**). Oil. – IR.: 1455, 1380, 1365. – ^{1}H-NMR.: 0.56, 0.85, and 0.90 (3*s*, 3 H, 6 H and 3 H, H_3C(18), H_3C(19) and 2 H_3C–C(4)); 5.20 (*m*, H–C(7)). – MS.: 286 (M^+, 10), 271 (10), 162 (100).

General preparation of the epoxides **56–60**. The olefin (100 mg) was dissolved in dry ether (40 ml) and treated with *m*-chloroperbenzoic acid (1.1 mol equiv.) at RT. for about 2 h (TLC. check). After normal work-up with Na_2SO_3-solution and brine the crude mixture was purified by chromatography on silicagel.

Acid catalyzed rearrangement of the 7α,8α-epoxides to the allylic alcohols. The epoxide (100 mg) was dissolved in dry $CHCl_3$ (about 40 ml). A dry solution of HCl in $CHCl_3$ (*ca.* 0.1N, 0.1 ml) was added and the mixture stirred for 15 min at RT. After normal work-up the isomeric allylic alcohols were separated by chromatography on silicagel.

3β,19:7α,8α-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-17β-ol acetate (**56**). M.p. 156°, $[\alpha]_D = -25°$ ($c = 0.60$). – IR.: 1725, 1382, 1373, 1363, 1333, 1250, 1150, 1120, 1102, 1095, 1070, 1066, 1037, 1013, 975, 961, 892. – ^{1}H-NMR.: 0.94, 0.99 and 1.09 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.04 (*s*, CH_3COO); 2.98 (*t*, $J = 2$, H–C(7)); 3.22 (*s*, CH_3O); 3.73 (br. *d*, $J = 9$, 1 H–C(19)); 3.88 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.70 (br. *t*, $J = 6$, H–C(17)). – MS.: 404 (M^+, 11), 386 (32), 343 (22), 326 (46), 283 (38), 270 (46), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.24 H 8.97%

3β,19:7α,8α-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-17α-ol acetate (**57**). M.p. 136°, $[\alpha]_D = -23°$ ($c = 0.95$). – IR.: 1725, 1458, 1438, 1385, 1372, 1335, 1320, 1300, 1250, 1156, 1145, 1125, 1100, 1071, 1035, 1020, 979, 964, 920, 902, 890, 850. – ^{1}H-NMR.: 0.94, 0.98 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.99 (*s*, CH_3COO); 2.97 (*t*, $J = 2$, H–C(7)); 2.21 (*s*, CH_3O); 3.70 (br. *d*, $J = 9$, 1 H–C(19)); 3.83 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.28 (*t*, $J = 4$, H–C(17)). – MS.: 404 (M^+, 5), 386 (88), 343 (38), 326 (48), 311 (33), 299 (30), 283 (63), 270 (68), 197 (88), 196 (75), *183* (100), 155 (65), 43 (78).

$C_{25}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.43 H 9.13%

3,19:7α,8α-Diepoxy-3α-methoxy-4,4-dimethyl-5α-androstan-17β-ol acetate (**58**). M.p. 225°, $[\alpha]_D = +29°$ ($c = 1.55$). – IR.: 1730, 1387, 1375, 1364, 1345, 1320, 1285, 1252, 1160, 1130, 1108, 1088, 1077, 1038, 980, 920, 900, 880. – ^{1}H-NMR.: 0.75, 0.93 and 0.95 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.00 (*s*, CH_3COO); 3.21 (*s*, CH_3O); 3.35 (br. *d*, H–C(7)); 3.85 (*m*, 2 H–C(19)); 4.65 (*m*, H–C(17)). – MS.: 404 (M^+, 17), 386 (25), 343 (23), 299 (42), 255 (43), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.18 H 9.98%

17β,19-Diacetoxy-7α,8α-epoxy-4,4-dimethyl-5α,13α-androstan-3-one (**59**). $[\alpha]_D = -36°$ ($c = 3.25$). – IR.: 1725, 1710, 1455, 1378, 1245, 1132, 1108, 1060, 1038, 1020, 980, 965, 912, 878. – ^{1}H-NMR.: 1.08 and 1.13 (2*s*, 3 H and 6 H, resp. 2 H_3C–C(4) and H_3C(18)); 2.04 and 2.06 (2*s*, CH_3COO); 3.06 (*m*, H–C(7)); 4.18 and 4.54 (*d*×*d*, $J = 12$, 2 H–C(19)); 4.77 (*m*, H–C(17)). – MS.: 432 (M^+, 27), *372* (100), 312 (37), 299 (37), 281 (53), 43 (53).

3β,19:7β,8β-Diepoxy-3α-methoxy-4,4-dimethyl-5α,13α-androstan-17α-ol acetate (**61**). M.p. 144°, $[\alpha]_D = -34°$ ($c = 0.95$). – IR.: 1730, 1460, 1440, 1385, 1375, 1363, 1335, 1317, 1255, 1162, 1147, 1106, 1091, 1074, 1038, 970, 965, 930, 909, 898, 858, 847, 830. – ^{1}H-NMR.: 0.92, 0.96 and 0.98 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.99 (*s*, CH_3COO); 3.06 (*d*×*d*, $J = 4$, $J' = 3$, H–C(7)); 3.20 (*s*, CH_3O); 3.56 (*d*×*d*, $J = 10$, $J' = 2$, 1 H–C(19)); 4.23 (*d*×*d*, $J = 10$, $J' = 3$, 1 H–C(19)); 5.09 (br. *t*, $J = 8$, H–C(17)). – MS.: 404 (M^+, 15), 361 (29), 335 (36), 334 (31), *333* (100), 321 (81), 317 (40), 275 (60), 261 (47), 257 (49), 243 (44), 215 (40), 197 (44), 43 (89).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.25 H 8.99%

17β,19-Diacetoxy-7α-hydroxy-4,4-dimethyl-5α-androst-8-en-3-one (**62**). $[\alpha] = +121°$ ($c = 3.55$). – IR.: 3600, 1732, 1710 sh, 1460, 1387, 1372, 1250, 1130, 1035, 978, 948, 915. – ^{1}H-NMR.: 0.70 (*s*, H_3C(18)); 1.04 and 1.14 (2*s*, 2 H_3C–C(4)); 1.97 and 2.02 (2*s*, 2 CH_3COO); 3.94 and 4.24 (2*d*, $J = 12$, 2 H–C(19)); 4.16 (*m*, H–C(7)); 4.69 (*m*, H–C(17)). – MS.: 432 (M^+, 4), 372 (60), 364 (56), 302 (28), 299 (32), 281 (36), 274 (33), *43* (100).

17β,19-Diacetoxy-7α-hydroxy-4,4-dimethyl-5α-androst-8(14)-en-3-one (**63**). $[\alpha]_D = -60°$ ($c = 2.85$). – IR.: 3600, 1730, 1705, 1455, 1435, 1373, 1245, 1130, 1065, 1038, 1030, 1010, 908, 838. – ^{1}H-NMR.: 0.94 (*s*, H_3C(18)); 1.09 and 1.13 (2*s*, 2 H_3C–C(4)); 2.03 (*s*, 6 H, 2 CH_3COO); 4.03 and 4.44 (2*d*, $J = 12$, 2 H–C(19)); 4.62 (*m*, 2 H, H–C(7) and H–C(17)). – MS.: *432* (M^+, 100), 372 (23), 281 (22), 221 (35), 176 (46), 161 (29), 43 (37).

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-7α-ol (**64**). M.p. 185° (decomp.), $[\alpha]_D = +98°$ ($c = 1.10$). – IR.: 3600, 1722, 1468, 1446, 1430, 1385, 1375, 1363, 1332, 1250, 1145, 1140, 1122, 1091, 1070, 1052, 1020, 1004, 980, 932, 908, 887, 849. – ^{1}H-NMR.: 0.90, 0.96 and 1.00 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.01 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.79 (*d*×*d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.92 (*d*, $J = 9$, 1 H–C(19)); 3.94 (*m*, H–C(7)); 4.83 (*m*, H–C(17)). – MS.: 404 (M^+, 21), 386 (18), 343 (21), 326 (28), 270 (96), 215 (75), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.28 H 9.06%

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-7α-ol (**65**). $[\alpha]_D = -24°$ ($c = 0.90$). – IR.: 3605, 1720, 1460, 1373, 1332, 1250, 1158, 1145, 1120, 1096, 1075, 1035, 1025, 1010, 968, 900, 888. – ^{1}H-NMR.: 0.90, 0.92 and 1.01 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.97 (*s*, CH_3COO); 3.22 (*s*, CH_3O); 3.76 (*d*, $J = 9$, 1 H–C(19)); 3.88 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.64 (*t*, $J = 3$, H–C(7)); 4.92 (*d*, $J = 4$, H–C(17)). – MS.: 404 (M^+, 7), 386 (44), 326 (70), *43* (100).

17α-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-7α-ol (**66**). M.p. 176°, $[\alpha]_D = +62°$ ($c = 1.75$). – IR.: 3610, 1720, 1470, 1375, 1335, 1305, 1255, 1145, 1125, 1094, 1070, 1050, 1032, 1010, 980, 970, 938, 910, 890, 856. – ^{1}H-NMR.: 0.83, 0.96 and 1.01 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.02 (*s*, CH_3COO); 3.27 (*s*, CH_3O); 3.78 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 3.90 (*d*, $J = 9$, 1 H–C(19)); 3.99 (*m*, H–C(7)); 3.81 (*m*, H–C(17)). – MS.: 404 (M^+, 17), 386 (57), 343 (45), 326 (51), 311 (30), 299 (43), 283 (68), 270 (85), 197 (62), 183 (72), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.06 H 9.15%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-7α,17α-diol diacetate (**68**). IR.: 1725, 1465, 1435, 1373, 1335, 1294, 1250, 1146, 1112, 1080, 1057, 1044, 1032, 1019, 940, 922, 900, 874, 856. – ^{1}H-NMR.: 0.87, 0.89 and 1.00 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.02 (*s*, 6 H, 2 CH_3COO); 3.22 (*s*, CH_3O); 3.74 (*m*, $w_{1/2} = 4$, 2 H–C(19)); 4.52 (*m*, H–C(17)); 5.67 (*m*, H–C(7)). – MS.: 446 (M^+, < 1), 386 (5), 326 (5), 273 (4), 225 (16), 197 (13), 183 (16), *43* (100).

17β,19-Diacetoxy-7α-hydroxy-4,4-dimethyl-5α,13α-androst-8-en-3-one (**69**). M.p. 182°, $[\alpha]_D = +111°$ ($c = 3.15$). – IR.: 3605, 1725, 1710 sh, 1460, 1385, 1368, 1245, 1148, 1055, 1040, 985, 921. – ^{1}H-NMR.: 0.95, 1.06 and 1.14 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.96 and 2.02 (2*s*, 2 CH_3COO); 3.90 and 4.33 (2*d*, $J = 12$, 2 H–C(19)); 4.04 (*m*, H–C(7)); 4.84 (*m*, H–C(17)). – MS.: 432 (M^+, 13), 372 (91), 355 (36), 312 (62), 299 (55), 295 (44), 281 (87), *43* (100).

$C_{25}H_{36}O_6$ (432.54) Calc. C 69.42 H 8.39% Found C 69.25 H 8.42%

17β,19-Diacetoxy-7α-hydroxy-4,4-dimethyl-5α,13α-androst-8(14)-en-3-one (**70**). M.p. 173°, $[\alpha]_D = -22°$ ($c = 0.90$). – IR.: 3600, 1730, 1710 sh, 1455, 1430, 1375, 1305, 1250, 1130, 1095, 1078, 1048, 1028, 1010, 980, 970, 920 br., 880, 855, 835. – ^{1}H-NMR.: 0.97, 1.05 and 1.13 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.97 and 1.99 (2*s*, 2 CH_3COO); 3.98 and 4.29 (2*d*, $J = 12$, 2 H–C(19)); 4.70 (*m*, on treatment with D_2O, *t*, $J = 3$, H–C(7)); 4.95 (*d*, $J = 4$, H–C(17)). – MS.: 432 (M^+, < 1), 372 (34), 357 (16), 354 (22), 294 (12), 281 (15), *43* (100).

$C_{25}H_{36}O_6$ (432.54) Calc. C 69.42 H 8.39% Found C 69.51 H 8.45%

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8-en-7α-ol (**71**). M.p. 172°, $[\alpha]_D = +129°$ ($c = 1.35$). – IR.: 3610, 1725, 1470, 1388, 1375, 1365, 1345, 1282, 1255, 1155 sh, 1145, 1125, 1110, 1100, 1090, 1033, 970, 950, 935, 905, 882. – ^{1}H-NMR.: 0.66 (*s*, H_3C(18)); 0.95 and 1.00 (2*s*, 2 H_3C–C(4)); 2.02 (*s*, CH_3COO); 3.27 (*s*, CH_3O); 3.77 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 3.91 (*d*, $J = 9$, 1 H–C(19)); 4.06 (*m*, H–C(7)); 4.66 (*m*, H–C(17)). – MS.: 404 (M^+, 27), 386 (45), 334 (57), *299* (100), 43 (91).

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8(14)-en-7α-ol (**72**). M.p. 205°, $[\alpha]_D = -57°$ ($c = 1.05$). – IR.: 3600, 1728, 1459, 1435, 1372, 1330, 1295, 1250, 1150, 1138, 1123, 1100, 1090, 1070, 1039, 975, 920, 900, 850. – ^{1}H-NMR.: 0.87, 0.91 and 1.03 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.03 (*s*, CH_3COO); 3.23 (*s*, CH_3O); 3.71 (*d*×*d*, $J = 9$, $J' = 3$, 1 H–C(19)); 3.85 (*d*, $J = 9$, 1 H–C(19)); 4.46–4.68 (*m*, 2 H, H–C(17) and H–C(7)). – MS.: 404 (M^+, 77), 386 (57), 335 (50), 326 (65), 316 (67), 293 (56), *43* (100).

$C_{24}H_{36}O_5$ (404.53) Calc. C 71.25 H 8.97% Found C 71.12 H 9.04%

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-7,9(11)-dien-17β-ol acetate (**74**). M.p. 158–160°, $[\alpha]_D = +85°$ ($c = 0.75$). – UV.: 237 (8270), 243 (8830), 250 sh (6410). – IR.: 1725, 1470, 1386, 1375, 1362, 1335, 1255, 1145, 1116, 1088, 1035, 978, 908. – ^{1}H-NMR.: 0.52 (*s*, $H_3C(18)$); 0.98 and 1.00 (2*s*, 2 H_3C–C(4)); 2.02 (*s*, CH_3COO); 3.26 (*s*, CH_3O); 3.57 (*d* ×*d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.88 (*d* × *d*, $J = 9$, $J' = 3$, 1 H–C(19)); 4.75 (*m*, H–C(17)); 5.51 (*m*, 2 H, H–C(7) and H–C(11)). – MS.: 386 (M^+, 65), 343 (17), 326 (31), 298 (30), 283 (30), 270 (31), 255 (56), 223 (41), 183 (63), *93* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-7,14-dien-17β-ol (**75**). M.p. 178–180°. – UV.: 247 (22,028). – IR.: 3615, 1468, 1386, 1365, 1334, 1302, 1275, 1158, 1140, 1135, 1120, 1108, 1095, 1070, 1035, 1000, 990, 975, 922, 908, 878, 850. – ^{1}H-NMR.: 0.87, 0.95 and 1.06 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 3.26 (*s*, CH_3O); 3.60 (*m*, H–C(17)); 3.70 (*m*, $w_{1/2} = 4$, 2 H–C(19)); 5.57 and 6.21 (2*d* × *d*, $J = 10$, $J' = 3$, H–C(7) and H–C(15)). – MS.: *344* (M^+, 100), 301 (42), 257 (44).

3,19-Epoxy-3α-methoxy-4,4-dimethyl-5α-androst-7,9(11)-dien-17β-ol (**76**). M.p. 226–228°, $[\alpha]_D = +126°$ ($c = 1.35$). – UV.: 239 sh (12,765), 244 (13,300), 252 sh (10,020). – IR.: 3610, 1470, 1387, 1376, 1363, 1335, 1145, 1115, 1088, 1070, 1045, 935, 910. – ^{1}H-NMR.: 0.51 (*s*, $H_3C(18)$); 0.98 and 1.00 (2*s*, 2 H_3C–C(4)); 3.26 (*s*, CH_3O); 3.58 (*d* × *d*, $J = 9$, $J' = 2$, 1 H–C(19)); 3.78 (*m*, H–C(17)); 3.87 (*d* × *d*, $J = 9$, $J' = 3$, 1 H–C(19)); 5.52 (*m*, 2 H, H–C(7) and H–C(11)). – MS.: *344* (M^+, 100), 301 (27), 288 (45), 229 (64).

17β,19-Diacetoxy-4,4-dimethyl-5α,13α-androst-8-en-3,7-dione (**77**). $[\alpha]_D = +34°$ ($c = 1.25$). – UV.: 246 (9694). – IR.: 1725 br., 1660, 1615, 1460, 1420, 1378, 1250, 1110, 1055 sh, 1045, 1020, 995, 915. – ^{1}H-NMR.: 0.88, 1.13 and 1.18 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.96 and 2.02 (2*s*, 2 CH_3COO); 4.22 and 4.68 (2*d*, $J = 12$, 2 H–C(19)); 4.87 (*t*, $J = 8$, H–C(17)). – MS.: 430 (M^+, 48), *370* (100), 318 (40), 297 (43), 213 (45), 84 (48), 43 (90).

17β,19-Diacetoxy-4,4-dimethyl-5α-androst-8-en-3,7-dione (**78**). M.p. 172°, $[\alpha]_D = -16°$ ($c = 1.40$). – UV.: 250 (8620). – IR.: 1732, 1715, 1665, 1582, 1460, 1421, 1388, 1375, 1360, 1320, 1310, 1250, 1132, 1112, 1038, 998, 942, 910. – ^{1}H-NMR.: 0.72 (*s*, $H_3C(18)$); 1.12 (*s*, 6 H, 2 H_3C–C(4)); 2.02 (*s*, 6 H, 2 CH_3COO); 4.21 and 4.61 (2*d*, $J = 12$, 2 H–C(19)); 4.68 (*m*, H–C(17)). – MS.: 430 (M^+, 95), 388 (10), 370 (31), *43* (100).

$C_{25}H_{34}O_6$ (430.52) Calc. C 69.74 H 7.96% Found C 69.64 H 7.96%

17β,19-Diacetoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-3,7-dione (**79**). UV.: 257 (6346). – IR.: 1732, 1715, 1672, 1598, 1455, 1375, 1245, 1037, 968, 940, 905. – ^{1}H-NMR.: 1.01, 1.11 and 1.14 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.92 and 1.96 (2*s*, 2 CH_3COO); 4.27 and 4.50 (2*d*, $J = 12$, 2 H–C(19)); 4.97 (*d*, $J = 4$, H–C(17)). – MS.: 430 (M^+, 3), *370* (100), 43 (48).

17β,19-Diacetoxy-4,4-dimethyl-5α-androst-8(14)-en-3,7-dione (**80**). M.p. 128–130°, $[\alpha]_D = -63°$ ($c = 0.925$). – UV.: 260 (10,814). – IR.: 1735, 1710, 1675, 1600, 1460, 1390, 1374, 1250, 1154, 1130, 1062, 1040, 990, 970, 949, 910. – ^{1}H-NMR.: 1.02, 1.08 and 1.14 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.94 and 2.05 (2*s*, 2 CH_3COO); 4.22 and 4.66 (2*d*, $J = 12$, 2 H–C(19)); 4.72 (*m*, H–C(17)). – MS.: 430 (M^+, 2), 388 (4), *370* (100), 43 (31).

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-7-one (**81**). M.p. 183°, $[\alpha]_D = +63°$ ($c = 0.90$). – UV.: 249 (8380). – IR.: 1730, 1678, 1616, 1465, 1420, 1382, 1375, 1364, 1335, 1250, 1140 br. 1110, 1090, 1055, 1025, 978, 920, 905. – ^{1}H-NMR.: 0.86, 0.88 and 0.89 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.01 (*s*, CH_3COO); 3.28 (*s*, CH_3O); 4.05 (*m*, 2 H–C(19)); 4.87 (br. *t*, $J = 7$, H–C(17)). – MS.: *402* (M^+, 100), 360 (14), 342 (46), 299 (33), 286 (58), 273 (50), 213 (92), 43 (96).

$C_{24}H_{34}O_5$ (402.51) Calc. C 71.61 H 8.51% Found C 71.69 H 8.58%

17α-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8-en-7-one (**82**). M.p. 168°, $[\alpha]_D = +60°$ ($c = 1.10$). – UV.: 249 (9990). – IR.: 1720, 1662, 1615, 1470, 1448, 1425, 1383, 1374, 1338, 1310, 1255, 1155 sh, 1138, 1112, 1090, 1052, 1040, 1029, 988, 976, 923, 909. – ^{1}H-NMR.: 0.79, 0.98 and 1.00 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.02 (*s*, CH_3COO); 3.28 (*s*, CH_3O); 3.98 (*d* × *d*, $J = 9$, $J' = 1$, 1 H–C(19)); 4.10 (*d* × *d*, $J = 9$, $J' = 2$, 1 H–C(19)); 4.82 (*d* × *d*, $J = 6$, $J' = 3$, H–C(17)). – MS.: 402 (M^+, 77), 342 (58), 299 (35), 286 (54), 273 (73), *213* (100), 43 (73).

$C_{24}H_{34}O_5$ (402.51) Calc. C 71.61 H 8.51% Found C 71.64 H 8.49%

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8-en-7-one (**83**). M.p. 218°, $[\alpha]_D = -4°$ ($c = 0.75$). – UV.: 251 (9632). – IR.: 1725, 1670, 1595, 1470, 1422, 1390, 1376, 1360,

1348, 1320, 1255, 1141, 1112, 1098, 1045, 1030, 975, 938, 921, 905. – ^{1}H-NMR.: 0.66 (*s*, $H_3C(18)$); 0.97 and 0.99 (2*s*, 2 H_3C–C(4)); 2.02 (*s*, CH_3COO); 3.28 (*s*, CH_3O); 3.99 (*d*×*d*, $J=9$, $J'=1$, 1 H–C(19)); 4.13 (*d*×*d*, $J=9$, $J'=3$, 1 H–C(19)); 4.66 (br. *t*, $J=8$, H–C(17)). – MS.: *402* (M^+, 100), 359 (13), 346 (14), 315 (25), 273 (34), 213 (56), 185 (30), 43 (66).

$C_{24}H_{34}O_5$ (402.51) Calc. C 71.61 H 8.51% Found C 71.52 H 8.56%

17β-Acetoxy-3,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-7-one (**84**). M.p. 152°, $[\alpha]_D=-39°$ ($c=0.825$). – UV.: 253 (7932). – IR.: 1722, 1680, 1638, 1592, 1468, 1458, 1415, 1386, 1375, 1365, 1335, 1280, 1250, 1148, 1131, 1110, 1092, 1080, 1040, 968, 949, 916, 900. – ^{1}H-NMR.: 0.94, 0.99 and 1.04 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.97 (*s*, CH_3COO); 3.24 (*s*, CH_3O); 3.85 (*d*, $J=10$, 1 H–C(19)); 3.99 (*d*×*d*, $J=10$, $J'=3$, 1 H–C(19)); 4.96 (*d*, $J=4$, H–C(17)). – MS.: 402 (M^+, 5), 342 (64), 332 (96), 255 (36), *199* (100), 43 (56).

$C_{24}H_{34}O_5$ (402.51) Calc. C 71.60 H 8.51% Found C 71.78 H 8.50%

17α-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-7-one (**85**). M.p. 133–136°. – UV.: 251 (6542). – IR.: 1725, 1680, 1590, 1460 br., 1380 sh, 1370, 1335, 1310, 1250, 1149, 1100, 1088, 1040, 918, 900. – ^{1}H-NMR.: 0.92, 0.98 and 1.03 (3*s*, 2 $H_3C(4)$ and $H_3C(18)$); 2.05 (*s*, CH_3COO); 3.24 (CH_3O); 3.87 (*m*, 2 H–C(19)); 4.60 (*d*×*d*, $J=10$, $J'=8$, H–C(17)). – MS.: 402 (M^+, 20), 342 (44), 332 (95), 300 (23), 273 (36), 199 (48), *43* (100).

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-5α-androst-8(14)-en-7-one (**86**). M.p. 150°, $[\alpha]_D=-18°$ ($c=0.875$). – UV.: 254 (10,836). – IR.: 1730, 1680, 1620, 1462, 1375, 1335, 1250, 1158, 1140, 1125, 1100, 1087, 1040, 985, 920, 898. – ^{1}H-NMR.: 0.94, 0.95 and 0.99 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.03 (*s*, CH_3COO); 3.24 (*s*, CH_3O); 3.84 (*m*, $w_{1/2}=4$, 2 H–C(19)); 4.67 (*d*×*d*, $J=10$, $J'=8$, H–C(17)). – MS.: 402 (M^+, 6), 342 (39), *332* (100), 291 (23), 273 (39), 255 (25), 199 (48), 43 (39).

$C_{24}H_{34}O_5$ (402.51) Calc. C 71.61 H 8.51% Found C 71.52 H 8.53%

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α,13α-androst-8-en-3,7-dione (**87**). M.p. 172–173°. – UV.: 249 (8670). – IR.: 3595, 1720, 1658, 1612, 1375, 1365, 1248, 1145, 1135, 1085, 1055, 1014, 975, 910. – ^{1}H-NMR.: 0.86, 1.00 and 1.05 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 2.01 (*s*, CH_3COO); 4.06 (*m*, 2 H–C(19)); 4.87 (*m*, H–C(17)). – MS.: 388 (M^+, 26), 358 (18), 328 (62), 298 (38), *213* (100), 43 (54).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α-androst-8-en-3,7-dione (**88**). UV.: 252 (6114). – IR.: 3585, 1722, 1667, 1591, 1462, 1420, 1386, 1375, 1360, 1318, 1250, 1140, 1100, 1041, 970, 958, 935, 915, 905. – ^{1}H-NMR.: 0.64 (*s*, $H_3C(18)$); 0.99 and 1.05 (2*s*, 2 H_3C–C(4)); 2.01 (*s*, CH_3COO); 4.00 (*d*×*d*, $J=9$, $J'=2$, 1 H–C(19)); 4.12 (*d*×*d*, $J=9$, $J'=3$, 1 H–C(19)); 4.66 (*m*, H–C(17)). – MS.: *388* (M^+, 100), 358 (38), 328 (20), 315 (37), 297 (20), 273 (44), 213 (41), 43 (57).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α,13α-androst-8(14)-en-3,7-dione (**89**). UV.: 252 (6466). – IR.: 3590, 1725, 1680, 1595, 1465 br., 1373, 1245, 1070, 1045, 1035, 990, 965, 910, 898. – ^{1}H-NMR.: 0.98, 0.99 and 1.08 (3*s*, 2 H_3C–C(4) and $H_3C(18)$); 1.97 (*s*, CH_3COO); 3.93 (*m*, 2 H–C(19)); 5.95 (*d*, $J=4$, H–C(17)). – MS.: 388 (M^+, 5), *328* (100), 43 (23).

17β-Acetoxy-19-hydroxy-4,4-dimethyl-5α-androst-8(14)-en-3,7-dione (**90**). M.p. 137–139°, $[\alpha]_D=-10°$ ($c=0.30$). – UV.: 256 (8801). – IR.: 3585, 1728, 1680, 1620, 1463, 1372, 1245, 1145, 1110, 1040, 965, 917. – ^{1}H-NMR.: 0.97 and 1.03 (2*s*, 6 H and 3 H, resp. 2 H_3C–C(4) and $H_3C(18)$); 2.04 (*s*, CH_3COO); 3.72 (*m*, 2 H–C(19)); 4.67 (*d*×*d*, $J=10$, $J'=8$, H–C(17)). – MS.: 388 (M^+, 7), *328* (100), 259 (16), 199 (18), 43 (57).

General procedure for the cleavage of the Δ^8- *or* $\Delta^{8(14)}$-*double bond.* The seco-products were prepared by treatment of the olefins with RuO_4[31]) in CCl_4 at RT. for 15 min. The excess of reagent was destroyed with 2-propanol and the solution was filtered through *Celite*. The crude mixture was purified by chromatography on silicagel.

17β-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-8,9-seco-5α,13α-androstan-8,9-dione (**91**). M.p. 202°, $[\alpha]_D=+36°$ ($c=0.84$). – IR. ($CHCl_3$): 1723, 1690, 1467, 1420, 1376, 1365, 1330, 1318, 1285,

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[31]) Preparation of the CCl_4/RuO_4-solution [24]: A suspension of 0.4 g of hydrated RuO_2 in 50 ml of CCl_4 was stirred at 0° and treated for 1 h with a solution of 3.2 g of sodium metaperiodate in 50 ml of water.

1245, 1128, 1098, 1060, 1028, 1000, 975, 910, 884, 845. IR (CCl_4): 1738, 1694, 1420, 1362, 1235, 1130, 1098, 1064, 1033. – ^{1}H-NMR.: 1.00 and 1.13 (2*s*, 3 H and 6 H, resp., 2 H_3C–C(4) and H_3C(18)); 2.04 (*s*, CH_3COO); 3.24 (*s*, CH_3O); 3.93 and 4.19 (2*d*×*d*, J=9, J'=2, 2 H–C(19)); 4.68 (br. *t*, J=8, H–C(17)). – MS.: 420 (M^+, 9), 402 (18), 364 (13), 360 (12), 347 (18), 342 (16), 304 (19), 287 (27), 286 (33), 255 (49), *43* (100).

$C_{24}H_{36}O_6$ (420.53) Calc. C 68.54 H 8.63% Found C 68.43 H 8.46%

17α-Acetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-8,9-seco-5α,13α-androstan-8,9-dione (**92**). M.p. 159–161°, $[\alpha]_D$= +36° (c=1.00). – IR. (CCl_4): 1738, 1696, 1467, 1424, 1388, 1370, 1332, 1320, 1303, 1239, 1130, 1100, 1064, 1035. – ^{1}H-NMR.: 1.00, 1.07 and 1.14 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.02 (*s*, CH_3COO); 3.23 (*s*, CH_3O); 3.91 (*d*×*d*, J=10, J'=1, 1 H–C(19)); 4.19 (*d*×*d*, J=10, J'=2, 1 H–C(19)); 4.79 (*d*×*d*, J=6, J'=2, H–C(17)). – MS.: 420 (M^+, 9), 402 (25), 360 (27), 347 (18), 342 (22), 287 (27), *43* (100).

4,4-Dimethyl-8,9-seco-5α,13α-androstan-8,9-dione (**93**). IR. (CCl_4): 1688, 1452, 1420, 1360, 1315, 1295, 1245, 1190, 1128, 1090, 1038, 976. – ^{1}H-NMR.: 0.88, 1.11 and 1.12 (3*s*, 3 H, 6 H and 3 H, resp., H_3C(18), H_3C(19) and 2 H_3C–C(4)). – MS.: 318 (M^+, 24), 300 (22), 290 (63), 207 (88), *168* (100).

17β-Acetoxy-3,19-epoxy-3α-methoxy-4,4-dimethyl-8,14-seco-5α,13α-androstan-8,14-dione (**94**). IR. (CCl_4): 1735 sh, 1730, 1713 sh, 1388, 1375, 1338, 1248, 1150, 1135, 1125, 1045, 970, 915. – ^{1}H-NMR.: 0.94, 1.02 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.12 (*s*, CH_3COO); 3.21 (*s*, CH_3O), 3.64 (*m*, $w_{1/2}$=5, 2 H–C(19)); 5.15 (*m*, H–C(17)). – MS.: 420 (M^+, 2), 402 (2), 364 (5), 360 (5), 265 (14), 83 (40), *69* (100), 43 (37).

17β-Acetoxy-3,19-epoxy-3α-methoxy-4,4-dimethyl-8,14-seco-5α-androstan-8,14-dione (**97**). M.p. 155–157°, $[\alpha]_D$= +9° (c=0.58). – IR.: 1735, 1713 sh, 1465, 1405, 1379, 1370, 1335, 1240, 1145, 1130, 1110 br., 1072, 1038 br., 990, 915, 910. – ^{1}H-NMR.: 0.94, 0.98 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.04 (*s*, CH_3COO); 3.21 (*s*, CH_3O); 3.48–3.76 (*m*, $w_{1/2}$=3, 2 H–C(19)); 5.20 (br. *t*, J=5, H–C(17)). – MS.: 420 (M^+, 9), 405 (4), 392 (5), 364 (23), 360 (12), 304 (14), 265 (38), 182 (30), 111 (36), *69* (100), 43 (35).

$C_{24}H_{36}O_6$ (420.53) Calc. C 68.54 H 8.63% Found C 68.55 H 8.71%

4,4-Dimethyl-8,14-seco-5α-androstan-8,14-dione (**99**). IR. (CCl_4): 1735, 1710, 1458, 1408, 1390, 1370, 1320, 1270, 1230, 1178, 1160, 1105, 1060 br., 968, 942. – ^{1}H-NMR.: 0.67, 0.82, 0.94 and 0.97 (4*s*, H_3C(18), H_3C(19) and 2 H_3C–C(4)). – MS.: 318 (M^+, 69), 303 (69), 221 (28), 220 (31), *179* (100).

3β,19-Epoxy-3α-methoxy-4,4-dimethyl-5α,13α-androst-8(14)-en-7α,17β-diol diacetate (**100**). M.p. 137°, $[\alpha]_D$= −23° (c=1.55). – IR.: 1722, 1460, 1375, 1336, 1305, 1250, 1160, 1145, 1120, 1075, 1065, 1037, 1020, 1000, 984, 970, 936, 899, 877, 853. – ^{1}H-NMR.: 0.89, 0.90 and 1.00 (3*s*, 2 H_3C–C(4) and H_3C(18)); 1.98 and 2.01 (2*s*, 2 CH_3COO); 3.22 (*s*, CH_3O); 3.77 (*d*, J=9, 1 H–C(19)); 3.89 (*d*×*d*, J=9, J'=2, 1 H–C(19)); 4.92 (*d*, J=4, H–C(17)); 5.61 (*m*, H–C(7)). – MS.: 446 (M^+, <1), 386 (15), 326 (20), 311 (16), 283 (28), 45 (50), *43* (100), 41 (37).

$C_{26}H_{38}O_6$ (446.56) Calc. C 69.93 H 8.58% Found C 69.94 H 8.59%

7α,17β-Diacetoxy-3β,19-epoxy-3α-methoxy-4,4-dimethyl-8,14-seco-5α,13α-androstan-8,14-dione (**101**). $[\alpha]_D$= +58° (c=0.90). – IR. (CCl_4): 1745, 1730 sh, 1460 br., 1435 br., 1410, 1385, 1373, 1338, 1285, 1235, 1195, 1152, 1125, 1070 sh, 1045, 1030, 970, 940, 916, 890. – ^{1}H-NMR.: 0.91, 1.01 and 1.06 (3*s*, 2 H_3C–C(4) and H_3C(18)); 2.10 and 2.12 (2*s*, 2 CH_3COO); 3.22 (*s*, CH_3O); 3.62 (*m*, 2 H–C(19)); 4.72 (*t*, J=3, H–C(17)); 5.15 (*m*, H–C(7)). – MS.: 478 (M^+, 5), 464 (5), 418 (16), 404 (12), 293 (33), 263 (26), 233 (30), *43* (100).

3β,19-Epoxy-8,17β-dihydroxy-3α-methoxy-4,4-dimethyl-8,14-seco-5α,13α-androst-8-en-7,14-dione (**102**). M.p. 207–210°. – UV.: 279 (8478). UV. (EtOH/traces of NaOH): 323. – IR.: 3520 br., 3430 br., 1745, 1673, 1648, 1467, 1458, 1392, 1375, 1330, 1302, 1288, 1274, 1171, 1156, 1144, 1117, 1090, 1074, 1050, 1030, 990, 980, 963, 919, 895, 870, 825. – ^{1}H-NMR.: 0.98, 1.00 and 1.02 (3*s*, 2 H_3C–C(4) and H_3C(18)); 3.28 (*s*, CH_3O); 3.98 (*m*, $w_{1/2}$=4, 2 H–C(19)); 4.22 (*m*, H–C(17)). – MS.: 392 (M^+, 18), 306 (8), 279 (6), 251 (9), 85 (59), *83* (100).

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