42. Stereochemical Aspects of Acid-Catalyzed Cyclopropane Ring-Opening Reactions. A Stereospecific Pathway to Crinosterol and Brassicasterol

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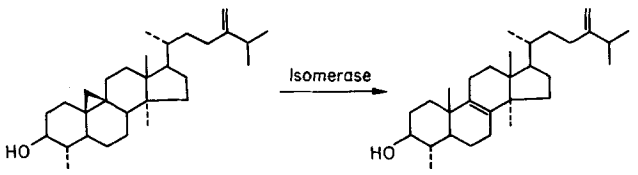
(6.XI.81)

Summary

It is shown that the acid-catalyzed ring-opening of the two diastereoisomeric 23,24-methylenecholesterols **3** and **5** on treatment with gaseous HCl in acetic acid leads stereospecifically to the naturally occurring crinosterol (**4**) and brassicasterol (**6**), respectively *(Scheme 1)*. This isomerization can be viewed as a biomimetic model of an *in vivo* methylation process of the type already known in plant sterol metabolism (*cf.* cycloeucalenol → obtusifoliol, **1** → **2**). The synthetic application of this method provides a convenient labelling of sterol side chains for tracer experiments. The mechanistic features of the reaction with respect to its particular stereospecificity are discussed.

Introduction. – Are sterols containing a cyclopropane ring moiety metabolic dead ends or do they represent biosynthetic intermediates? This question has become relevant with the recent isolation of many such sterols [1]. *Lederer* originally postulated [2] that cyclopropanes may serve as intermediates for methyl groups through a biochemical *reductive* opening, but he rejected this consideration on the basis of negative experimental results. However *in vivo* *C*-alkylation by *isomerization* of a cyclopropane intermediate to a methylated product (with an additional double bond) has been shown experimentally to be operative in plant sterol metabolism [3]. Thus cycloeucalenol (**1**) seems to play a key role in the biosynthesis of phytosterols since enzymatic opening of the three-membered ring leads to the Δ^8-isomer obtusifoliol (**2**) [4]. Therefore we considered the possibility of a similar enzymatic isomerization process occurring among cyclopropane-containing marine sterols [1].



1 **2**

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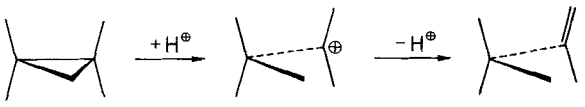
Our studies in the marine sterol field [5] and the recent discovery of various steroidal cyclopropanes (petrosterol [6], calysterol [7], gorgosterol [8], 23-demethylgorgosterol [9], and 22,23-methylenecholesterol [10]) prompted us to search for a possible biomimetic counterpart of such an enzymatic isomerization process. We recently published the results of our preliminary study in this direction [11]. The unique feature of having the cyclopropane ring in the side chain, which has been encountered only in marine, but not in terrestrial sterols, and which gives rise to much more conformational flexibility than nuclear cyclopropanes (*e.g.* **1**) induced us to examine the degree of stereospecificity of any anticipated ring-openings. We now report the details of the acid-catalyzed ring-opening of the diastereoisomeric 23,24-methylenecholesterols **3** and **5** *(Scheme 1)* which follows schematically the route **i**→**iii**, and leads unequivocally to the naturally occurring sterols crinosterol (**4**) and brassicasterol (**6**). Additionally we draw conclusions about a possible mechanism which may explain the unexpected regio- and stereospecificity of this isomerization.

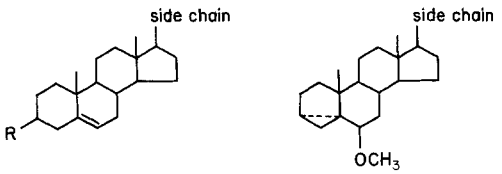


i ii iii

Scheme 1

3 (23*R*,24*S*) **4** (22*E*,24*S*)

5 (23*S*,24*R*) **6** (22*E*,24*R*)



A R=OH
B R=OAc
C R=Cl

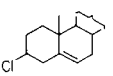
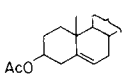
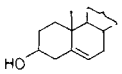
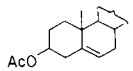
D

Results and discussion. – We previously reported [12] the synthesis of several model sterols containing diastereoisomerically pure, substituted three-membered rings in their side chain, of which the absolute configurations have been determined by either X-ray [13], spectroscopic (NMR.) and/or stereochemical correlations. Included were the synthesis and physical properties of the 23,24-methylene-cholesterol i-methyl ethers **7** and **14**, which we used as starting materials for the subsequent isomerization experiments described herein. Acid-catalyzed ring-openings using gaseous HCl in polar solvents have proved to be useful for different applications in the terpene [14] [15] as well as in the steroid series [11] [15] [16]. Under the same conditions, the i-methyl ether protecting group may also be transformed into the 3β-chloro Δ^5-system [13] [17]. Therefore we chose the i-methyl ethers as starting materials, since they represent an earlier precursor in the synthetic sequence compared to the corresponding acetates and free sterols.

To test the behavior of the Δ^5-system under the reaction conditions, the three cholesterol derivatives **iv–vi** *(Table 1)* were treated with gaseous HCl in glacial acetic acid for several hours at RT. and under reflux. The results of these experiments which were evaluated by GC./MS. are summarized in *Table 1*. In spite of the fact that the acetate **v** gave the best results, the direct transformation of the i-methyl ether **vi** to the corresponding 3β-chloro derivative **viii** at or below RT. offered a good HPLC. separation of the expected, relatively non-polar products.

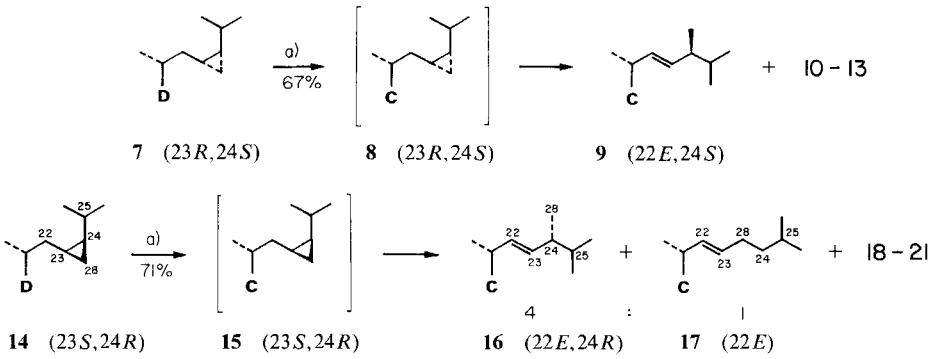
A 10^{-2}M solution of each of the i-methyl ethers **7** and **14** *(Scheme 2)* in glacial acetic acid was treated with gaseous HCl at RT. for 5 h, and the reaction monitored by GC. As expected, the starting material, **7** and **14**, was transformed during

Table 1. *Product analysis after treatment of three cholesterol derivatives* (**iv–vi**) *with gaseous HCl in acetic acid at RT. and under reflux* (rfl) *for 2 h*

		 vii	 viii	 v
 iv	RT.[a])	13	–	87
	rfl	23	12	65
 v	RT.	3	–	97
	rfl	23	11	66
 vi	RT.	10	88	2
	rfl[b])	15	55	30

[a]) After 3 h no starting material detected.
[b]) Product analysis after 3 h.

Scheme 2



[a]) HCl (gas)/HOAc; RT., 5 h.

a fast initial reaction step (30–45 min) into the corresponding 3β-chloro derivatives **8** and **15**. The side chain cyclopropane moiety in the initial products **8** and **15** could easily be recognized by GC./MS. analysis, because of the two diagnostic fragments at *m/z* 360 and 346 [12] ($M-C_4H_8$ and $M-C_5H_{10}$ respectively). In a subsequent slow reaction process, the GC. peak of the initial 3β-chloro steroidal cyclopropane diminishes in favor of an increasing peak with a somewhat shorter retention time but with the same mass spectral molecular ion as **8** and **15** respectively. Therefore we reran the whole experiment on a preparative scale and subjected the product mixture to separation by reverse-phase HPLC. The separation records of both ring-opening reactions starting from either diastereoisomeric steroidal cyclopropane **7** or **14** *(Scheme 2)* are reproduced in *Figure 1*. Owing to their spectroscopic properties (MS. and ^{1}H-NMR. spectra, see experimental part) the isolated HPLC. fractions *(Fig. 1)* can be divided into three categories. The first contains the anticipated 'true' isomers with an olefinic side chain (retention time (t_R) $\geqslant$ 160 min), the second deals with the products which originate from HCl addition (t_R 120–160 min), and the third corresponds to the steroids with an acetoxylated side chain (t_R 60–90 min).

Considering the isolated products starting from the i-methyl ether **7** (23*R*,24*S*), the only 'true' isomer detectable in the reaction mixture (67% yield) is the crinosterol derivative **9** (22*E*,24*S*). Its structural assignment could easily be done by comparison of the NMR. data with those of the well known crinosterol (**4**) and its acetate **23** (see *Table 2*). Definite constitutional assignment to the three chlorinated products **10–12** (all with molecular ions of *m/z* 452) was not feasible owing to some uncertainty because of the absence of reference data. Nevertheless we report their spectroscopic properties for completeness and emphasize that 3β-crinosteryl chloride (**9**) is the only 'true' isomer. More reliable, however, is the structure elucidation of the solely acetoxylated compound **13**. Its MS. – after loss of acetic acid – is identical with that of **9** and the complexity of the signal at 5.137 ppm (H–C(23)) in its ^{1}H-NMR. spectrum is consistent with the presence of three coupling partners, thus confirming the 23 position of the acetoxy group. In view of the correlation with crinosterol and the mechanistic considerations *(vide infra)*, the

absolute configuration of **13** at both chiral centers 23 and 24 has to be *S* as indicated in *Figure 1a.*

On the assumption that the acid-catalyzed ring-opening starting from the diastereoisomeric i-methyl ether **14** (23*S*,24*R*) should supply the C(24)-epimer of **9**, we assign the anticipated 3β-brassicasteryl chloride structure (**16**) to the first fraction (HPLC./t_R 185 min) of all isolated material (71%) as shown in *Figure 1b* and *Table 2.* In addition, an unexpected second 'true' isomer with a somewhat shorter HPLC. retention time (168 min) showed up as **17** (22*E*) (**16**/**17** = 4:1). Except for the latter's missing peak at *m/z* 373 ($M-C_3H_7$), the mass spectrum of both isomers **16** and **17** are almost superimposable, thus indicating that the position of the side chain double bond is the same. Its (*E*)-configuration is based on the ^{1}H-NMR. data. Comparison of the ^{1}H-NMR. spectra of **16** and **17** shows that a methyl group signal is missing in the spectrum of **17**. Therefore, we conclude that the side chain of **17** is homologous to that of 22-dehydrocholesterol. Indeed the side chain methyl group chemical shifts for both compound **17** and 22-dehydrocholesterol [18] are quite similar. As far as the products **18**–**20** are concerned *(Fig. 1b)*, they all show M^+ 452 in their MS. (see *Exper. Part*), but further constitutional assignments are related to the problems mentioned above for their isomeric counterparts *(Fig. 1a).* The spectroscopic properties of the shortest retention time fraction *(Fig. 1b)* and the mechanistic considerations *(vide infra)* require that the acetoxy 3β-chloro derivative **21** must be the (23*R*,24*R*)-diastereoisomer of **13** (23*S*,24*S*).

Since the isomerization of steroidal cyclopropanes might provide some preparative utility for the synthesis of specifically labelled material, we applied the same conditions to the corresponding acetates **22** and **28** *(Scheme 3).* In spite of

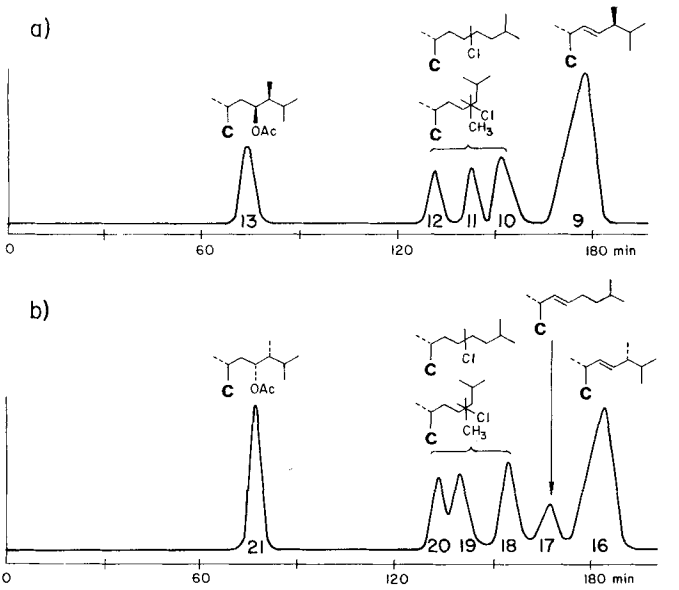


Fig. 1. *HPLC. of the reaction mixtures starting from* a) **7** *(23*R,*24*S*)* → **9**–**13** *and* b) **14** *(23*S,*24*R*)* → **16**–**21**

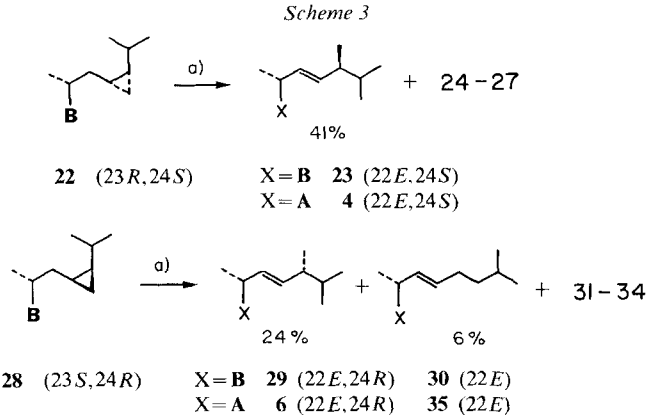
Table 2. *Selected[1] H-NMR.* (360 MHz, $CDCl_3$) *chemical shifts*[a])

Crinosterol derivatives (22*E*,24*S*)	**9** 3β-chloro	**23** 3β-acetoxy[b])	**4** 3β-hydroxy[c])
1 H–C(6)	5.368	5.375	5.349
2 H–C(22,23)	*5.158*	*5.160*	*5.162*
1 H–C(3)	3.77	4.60	3.53
3 H–C(19)	1.028	1.019	1.010
3 H–C(21)	*1.000 (6.63)*	*1.002 (6.68)*	*1.001 (6.20)*
3 H–C(28)	0.910 (6.84)	0.909 (6.78)	0.910 (6.86)
6 H–C(26,27)	0.834 (6.61)	0.835 (6.52)	0.836 (6.45)
	0.816 (6.66)	0.817 (6.63)	0.817 (6.62)
3 H–C(18)	0.689	0.690	0.693
Brassicasterol derivatives (22*E*,24*R*)	**16** 3β-chloro	**29** 3β-acetoxy[b])	**6** 3β-hydroxy[b])
1 H–C(6)	5.368	5.372	5.348
2 H–C(22,23)	*5.179*	*5.181*	*5.181*
1 H–C(3)	3.77	4.60	3.53
3 H–C(19)	1.028	1.020	1.010
3 H–C(21)	*1.009 (6.61)*	*1.011 (6.49)*	*1.011 (6.34)*
3 H–C(28)	0.909 (6.81)	0.910 (6.80)	0.910 (6.84)
6 H–C(26,27)	0.834 (5.81)	0.834 (6.5)	0.834 (6.10)
	0.817 (6.54)	0.818 (6.5)	0.817 (6.22)
3 H–C(18)	0.689	0.690	0.693

[a]) Given as δ values, (*J*) values in Hz. [b]) See *Exper. Part* and [18]. [c]) See *Exper. Part* and [19].

focusing primarily on the 'true' isomers **23**, **29** and **30**, we separated all by-products which were accessible by reverse-phase HPLC. The spectroscopic properties of the isolated compounds **23**–**27** and **29**–**34** (see *Exper. Part*) are in complete agreement with the above reported results in the 3β-chloro series. The yields of the analytically pure acetates of crinosterol **23**, brassicasterol **29** and the 22-dehydrocholesterol homolog **30** were 41%, 24% and 6%, respectively. Treatment of each acetate with lithium aluminium hydride provided the free sterols **4**, **6** and **35** *(Scheme 3)*.

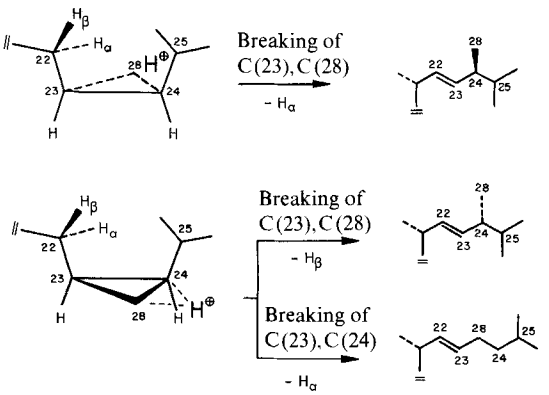
Scheme 3



[a]) HCl (gas)/HOAc; RT., 5 h.

Mechanistic considerations. – The remarkable regio- and stereospecific course of the above described acid-catalyzed cyclopropane-alkene isomerization merits some mechanistic consideration. Except for the thermally induced cyclopropane-propene isomerization, which seems to follow a concerted reaction pathway [20], practically no attention has been paid to the mechanistic features of olefin generation by electrophilic cyclopropane ring-opening. This may be due to the fact that the competition against nucleophilic attack on the initially generated carbonium ion under the present conditions is usually low; the olefinic 'by-products' in the hitherto published investigations [21] [22] are deliberately neglected. However as mentioned in the introduction, some interesting applications of such isomerization reactions are known, especially in natural product chemistry. Concerning the *in vivo* isomerization of **1**→**2**, which shows an unequivocal stereoselectivity in proton abstraction by chosing only one out of six possibilities, we note that with respect to the breaking cyclopropane bond, the only H-atom with a somewhat *syn*-periplanar arrangement (position 8 of cycloeucalenol (**1**)) is lost to form the 8(9)-double bond of obtusifoliol (**2**). Indeed, such a formal *syn*-elimination process – referring to the concerted fission of the cyclopropane C,C- and the adjacent C,H-bond – would also best explain our own observations about the electrophilic 23,24-methylenecholesterol cleavage. The fact that the only detectable olefins, which arise from a *Markovnikov* cleavage of the three-membered ring are crinosterol (**4**) and brassicasterol (**6**), strongly supports such a concerted, stereospecific olefin generation step. Based on this conclusion, any addition/elimination mechanism, which immediately would lead to other isomers, such as for example the Δ^{23}-analog, can be excluded. Even the occurrence of the homolog **35**, which accompanies brassicasterol (**6**), does not affect the accuracy of this statement, because this isomer results from an exceptional [23] anti-*Markovnikov* cleavage of the cyclopropane ring. Assuming the concerted C,C-bond fission/H-elimination to be correct, the initial protonation of the three-membered ring becomes the rate-determining step. This is consistent with the hitherto accepted mechanistic considerations about electrophilic cyclopropane ring-openings [21]. While these conclusions may explain

Scheme 4



the stereochemistry of the isomerization process, what is the answer to the unparalleled regiospecificity in our cyclopropanes which are capable of a fair degree of conformational flexibility? We attribute this to an unsymmetrically protonated three-membered ring [22] [24], which may be due to steric hindrance and which is especially notable in the case yielding the two isomeric compounds **6** and **35**. We summarize in *Scheme 4* all these mechanistic considerations, which may explain the reported cyclopropane-alkene isomerization. The absolute configurations which we assigned to the only detectable steroids having an acetoxylated side chain *(Fig. 1)* are based on the fact, that nucleophilic attack onto a protonated cyclopropane predominantly occurs under the present conditions with inversion of configuration [21].

Financial support by the *National Institutes of Health* (Grants No. GM-06840 and AM-04257) is gratefully acknowledged. In addition we thank Ms. *A. Wegmann* for mass spectral measurements and Dr. *L.J. Durham* for the 360-MHz NMR. spectra which were obtained at the Stanford NMR. facility funded by *NIH* Grant No. RR-0711 and *NSF* Grant No. GP-23633. We are especially indebted to Dr. *W.C.M.C. Kokke* for assistance in the HPLC. separations. *R.W.L.* thanks the *Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung* for a postdoctoral fellowship.

Experimental Part

General. Conditions and equipment used for the physical measurements in the synthetic section were those described in [12]. ^{1}H-NMR. (360 MHz): chemical shifts are given in ppm (TMS.) and coupling constants (J) in Hz. MS.: fragments (m/z) are given with relative intensity in parentheses. For separation of the mixtures *(cf. Fig. 1)*, high-performance liquid chromatography (HPLC. retention time = t_R) was carried out by using two *Altex Ultrasphere*™ ODS. columns 5 µm (10 mm i.d. × 25 cm) in series and abs. methanol as the mobile phase. The synthesis and the spectroscopic properties of the steroidal cyclopropanes **3** and **5** as well as of the i-methyl ethers **7** and **14** are described in [12].

Regeneration of the 3β-hydroxy-Δ^5-system from the 3β-acetoxy-Δ^5-system was accomplished generally by treatment of 5 mg of the acetate in 5 ml of dry ether with a 4-fold excess of $LiAlH_4$ at RT. for 30 min. The excess of the reagent was decomposed with saturated Na_2SO_4-solution, and after dilution with water, the free sterol was extracted with ether, dried ($MgSO_4$) and recrystallized from methanol after evaporation.

General procedure for the treatment of steroidal cyclopropanes with gaseous HCl in acetic acid. – The flexible part of the glass apparatus (gas connections) is constructed with teflon tubes. A silicon oil gas-bubbler for the HCl-stream monitoring (4–5 bubbles/s) is inserted. In a typical preparative run, 0.15 mmol of the steroidal cyclopropane were dissolved in 15 ml of glacial acetic acid (reagent grade) and treated with gaseous HCl (*Liquid Carbonic Corp.*, Chicago, Ill.) under constant stirring for 5 h at RT. The reaction was monitored by GC. (OV-17). Work-up was effected by dilution with water and extraction with ether. The organic layer was washed carefully with saturated $NaHCO_3$-solution, brine and water, dried ($MgSO_4$) and evaporated in a rotary evaporator. After filtration over silica gel (hexane/ethyl acetate 1:1) the reaction mixture was separated by HPLC.

Reaction of *7* with HCl in acetic acid. – The i-methyl ether **7** (55.0 mg, 0.133 mmol) was treated as described above. The reaction mixture was separated by HPLC. *(Fig. 1a)*. Five fractions **9**–**13** in a ratio 45:15:10:10:20 yielding together 67% were collected.

Fraction 1 (*(22E, 24S)-3β-Crinosteryl chloride*, **9**). M.p. 112–116° (MeOH); HPLC.: t_R 180 min. – ^{1}H-NMR.: 5.368 (*m*, 1H, H–C(6)); 5.158 (*m*, 2H, H–C(22) and H–C(23)); 3.77 (*m*, 1H, H_α–C(3)); 1.028 (*s*, 3H, H_3C(19)); 1.000 (*d*, J = 6.63, 3H, H_3C(21)); 1.910 (*d*, J = 6.84, 3H, H_3C(28)); 0.834 (*d*, J = 6.61, 3H) and 0.816 (*d*, J = 6.66, 3H), H_3C(26) and H_3C(27)); 0.689 (*s*, 3H, H_3C(18)). – HRMS.: 416.3220 (86, M^+, Calc. for $C_{28}H_{45}Cl$ 416.3207); 401.2965 (10, $C_{27}H_{42}Cl$, $M-CH_3$); 380.3456 (6, $C_{28}H_{44}$, M–HCl); 373.2708 (15, $C_{25}H_{38}Cl$, $M-C_3H_7$); 332.2280 (10, $C_{22}H_{33}Cl$, $M-C_6H_{12}$);

318.2127 (67, $C_{21}H_{31}Cl$); 303.1881 (15, $C_{20}H_{28}Cl$); 291.1836 (58, $C_{19}H_{28}Cl$); 289.1729 (54, $C_{19}H_{26}Cl$); 276.1642 (17, $C_{18}H_{25}Cl$); 255.2108 (8, $C_{19}H_{27}$); 251.1499 (6, $C_{16}H_{24}Cl$); 249.1393 (12, $C_{16}H_{22}Cl$); 69.0702 (100, C_5H_9).

Fraction 2 (**10**). M.p. 135–138° (MeOH); HPLC.: t_R 156 min. – ^{1}H-NMR.: 5.373 (*m*, 1H, H–C(6)); 4.112 (*m*, 1H, CHCl); 3.77 (*m*, 1H, H_a–C(3)); 1.032 (*s*, 3H, H_3C(19)); 0.942 (*d*, *J* = 7, 3H, H_3C(21)); 0.922 (*d*, *J* = 6.97, 3H, H_3C(28)); 0.910 (*d*, *J* = 6.88, 3H) and 0.864 (*d*, *J* = 6.70, 3H) H_3C(26) and H_3C(27)); 0.724 (*s*, 3H, H_3C(18)). – MS.: 452 (44, M^+), 437 (8, $M-CH_3$), 416 (20, $M-HCl$), 401 (5), 380 (6, $M-2HCl$), 349 (12), 332 (12), 323 (24), 318 (36), 303 (12), 291 (86), 289 (40), 276 (10), 264 (18), 255 (16), 251 (40), 249 (100), 235 (18), 213 (28).

Fraction 3 (**11**). M.p. 123–130° (MeOH); HPLC.: t_R 147 min. – ^{1}H-NMR.: 5.370 (*m*, 1H, H–C(6)); 4.358 (*m*, 1H, CHCl); 3.77 (*m*, 1H, H_a–C(3)); 1.028 (*s*, 3H, H_3C(19)); 0.955 (*d*, *J* = 6.46, 3H, H_3C(21)); 0.945 (*d*, *J* = 6.50, 3H, H_3C(28)); 0.945 (*d*, *J* = 6.50, 3H) and 0.919 (*d*, *J* = 6.62, 3H, H_3C(26) and H_3C(27)); 0.688 (*s*, 3H, H_3C(18)). – MS.: 452 (20, M^+), 437 (3, $M-CH_3$), 416 (20, $M-HCl$), 401 (4), 380 (10, $M-2HCl$), 349 (5), 332 (55), 319 (36), 313 (42), 303 (6), 291 (60), 289 (100), 276 (6), 264 (15), 255 (13), 251 (36), 249 (85), 235 (18), 213 (33).

Fraction 4 (**12**). HPLC.: t_R 133 min. – ^{1}H-NMR.: 5.369 (*m*, 1H, H–C(6)); 4.013 (*m*, 1H, CHCl); 3.77 (*m*, 1H, H_a–C(3)); 1.027 (*s*, 3H, H_3C(19)); 0.962 (*d*, *J* = 6.25, 3H, H_3C(21)); 0.910 (*d*, *J* = 6.54, 3H) and 0.892 (*d*, *J* = 6.54, 3H, H_3C(26) and H_3C(27)); 0.691 (*s*, 3H, H_3C(18)). – MS.: 452 (53, M^+), 437 (12, $M-CH_3$), 416 (12, $M-HCl$), 401 (5), 380 (11, $M-2HCl$), 349 (16), 323 (31), 318 (21), 303 (5), 291 (89), 289 (45), 277 (7), 264 (34), 255 (30), 251 (70), 249 (100), 235 (28), 213 (55).

Fraction 5 ((23S,24S)-23-Acetoxy-3β-chloro-24-methylcholest-5-ene, **13**). M.p. 144–148° (MeOH); HPLC.: t_R 78 min. – ^{1}H-NMR.: 5.366 (*m*, 1H, H–C(6)); 5.137 (*m*, 1H, H–C(23)); 3.77 (*m*, 1H, H_a–C(3)); 2.004 (*s*, 3H, $COCH_3$); 1.025 (*s*, 3H, H_3C(19)); 0.981 (*d*, *J* = 6.41, 3H, H_3C(21)); 0.904 (*d*, *J* = 6.91, 3H, H_3C(28)); 0.885 (*d*, *J* = 6.89, 3H) and 0.881 (*d*, *J* = 6.95, 3H, H_3C(26) and H_3C(27)); 0.679 (*s*, 3H, H_3C(18)). – MS.: 476 (not detectable, M^+), 440 (3, $M-HCl$), 416 (67, $M-HOAc$), 401 (12, $416-CH_3$), 380 (4), 373 (4), 332 (20), 318 (100), 303 (29), 289 (70), 276 (26), 264 (18), 249 (53), 235 (15), 233 (14), 213 (28).

Reaction of *14* with HCl in acetic acid. – The i-methyl ether **14** (55.0 mg, 0.133 mmol) was treated as described above. The mixture was separated by HPLC. *(Fig. 1b)*. Six fractions **16**–**21** in a ratio 27:9:14:12:14:24 yielding together 71% were collected.

Fraction 1 ((22E,24R)-3β-Brassicasteryl chloride, **16**). M.p. 134° (MeOH); HPLC.: t_R 185 min. – ^{1}H-NMR.: 5.368 (*m*, 1H, H–C(6)); 5.179 (*m*, 2H, H–C(22) and H–C(23)); 3.77 (*m*, 1H, H_a–C(3)); 1.028 (*s*, 3H, H_3C(19)); 1.009 (*d*, *J* = 6.61, 3H, H_3C(21)); 0.909 (*d*, *J* = 6.81, 3H, H_3C(28)); 0.834 (*d*, *J* = 5.81, 3H) and 0.817 (*d*, *J* = 6.54, 3H, H_3C(26) and H_3C(27)); 0.689 (*s*, 3H, H_3C(18)). – HRMS.: 416.3181 (81, M^+, Calc. for $C_{28}H_{45}Cl$ 416.3207); 401.2967 (9, $C_{27}H_{42}Cl$, $M-CH_3$); 380.3432 (12, $C_{28}H_{44}$, $M-HCl$); 373.2680 (13, $C_{25}H_{38}Cl$, $M-C_3H_7$); 332.2263 (13, $C_{22}H_{33}Cl$, $M-C_6H_{12}$); 318.2121 (55, $C_{21}H_{31}Cl$); 303.1879 (14, $C_{20}H_{28}Cl$); 291.1825 (53, $C_{19}H_{28}Cl$); 289.1719 (51, $C_{19}H_{26}Cl$); 276.1648 (15, $C_{18}H_{25}Cl$); 255.2097 (7, $C_{19}H_{27}$); 251.1374 (3, $C_{16}H_{24}Cl$); 249.1372 (11, $C_{16}H_{22}Cl$); 69.0706 (100, C_5H_9).

Fraction 2 ((22E)-3β-Chloro-23-homocholesta-5,22-diene, **17**). M.p. 130–132° (MeOH); HPLC.: t_R 168 min. – ^{1}H-NMR.: 5.367 (*m*, 1H, H–C(6)); 5.245 (*m*, 2H, H–C(22) and H–C(23)); 1.027 (*s*, 3H, H_3C(19)); 0.997 (*d*, *J* = 6.62, 3H, H_3C(21)); 0.865 (*d*, *J* = 6.55, 3H) and 0.862 (*d*, *J* = 6.68, 3H, H_3C(26) and H_3C(27)); 0.689 (*s*, 3H, H_3C(18)). – HRMS.: 416.3287 (64, M^+, Calc. for $C_{28}H_{45}Cl$ 416.3207); 401.2922 (13, $C_{27}H_{42}Cl$, $M-CH_3$); 380.3464 (9, $C_{28}H_{44}$, $M-HCl$); 318.2086 (81, $C_{21}H_{31}Cl$); 291.1840 (61, $C_{19}H_{28}Cl$); 289.1711 (36, $C_{19}H_{26}Cl$); 276.1638 (12, $C_{18}H_{25}Cl$); 255.2121 (9, $C_{19}H_{27}$); 249.1352 (12, $C_{16}H_{22}Cl$); 69.0703 (100, C_5H_9).

Fraction 3 (**18**). M.p. 137–140° (MeOH); HPLC.: t_R 154 min. – ^{1}H-NMR.: 5.371 (*m*, 1H, H–C(6)); 4.18 (*m*, 1H, CHCl); 3.77 (*m*, 1H, H_a–C(3)); 1.030 (*s*, 3H, H_3C(19)); 0.951 (*d*, *J* = 6.61, 3H, H_3C(21)); 0.951 (*d*, *J* = 6.61, 3H, H_3C(28)); 0.947 (*d*, *J* = 6.32, 3H) and 0.888 (*d*, *J* = 6.75, 3H, H_3C(26) and H_3C(27)); 0.720 (*s*, 3H, H_3C(18)). – MS.: 452 (46, M^+), 437 (7, $M-CH_3$), 416 (12, $M-HCl$), 401 (4), 380 (14), 349 (11), 332 (4), 325 (15), 323 (12), 318 (30), 303 (12), 291 (86), 289 (30), 276 (8), 264 (10), 255 (13), 251 (18), 249 (100), 235 (14), 213 (16).

Fraction 4 (**19**). HPLC.: t_R 140 min. – MS.: 452 (25, M^+), 437 (6, $M-CH_3$), 416 (3, $M-HCl$), 401 (2), 380 (1), 349 (6), 332 (3), 323 (10), 318 (8), 303 (5), 291 (34), 289 (17), 277 (6), 265 (15), 251 (35), 249 (100), 235 (12), 219 (8), 213 (18).

Fraction 5 (**20**). M.p. 136–142° (MeOH); HPLC.: t_R 134 min. – ^{1}H-NMR.: 5.369 (*m*, 1H, H–C(6)); 3.94 (*m*, 1H, CHCl); 3.77 (*m*, 1H, H_α–C(3)); 1.030 (*s*, 3H, $H_3C(19)$); 0.935 (*d*, *J* = 6.28, 3H, $H_3C(21)$); 0.896 (*d*, *J* = 6.52, 3H) and 0.887 (*d*, *J* = 6.54, 3H, $H_3C(26)$ and $H_3C(27)$); 0.718 (*s*, 3H, $H_3C(18)$). – MS.: 452 (47, M^+), 437 (13, $M-CH_3$), 416 (6, $M-HCl$), 401 (4), 380 (2), 349 (13), 323 (25), 303 (2), 291 (51), 277 (5), 264 (27), 251 (42), 249 (100), 235 (20), 213 (25).

Fraction 6 (*(23R, 24R)-23-Acetoxy-3β-chloro-24-methylcholest-5-ene*, **21**). M.p. 116–117° (MeOH); HPLC.: t_R 77 min. – ^{1}H-NMR.: 5.372 (*m*, 1H, H–C(6)); 5.086 (*m*, 1H, H–C(23)); 3.77 (*m*, 1H, H_α–C(3)); 2.039 (*s*, 3H, $COCH_3$); 1.024 (*s*, 3H, $H_3C(19)$); 0.955 (*d*, *J* = 6.93, 3H, $H_3C(21)$); 0.928 (*d*, *J* = 6.78, 3H, $H_3C(28)$); 0.820 (*d*, *J* = 6.73, 3H) and 0.813 (*d*, *J* = 6.93, 3H, $H_3C(26)$ and $H_3C(27)$); 0.658 (*s*, 3H, $H_3C(18)$). – MS.: 476 (not detectable, M^+), 440 (3, $M-HCl$), 416 (81, $M-HOAc$), 401 (9, $416-CH_3$), 380 (3), 373 (4), 332 (30), 318 (100), 303 (14), 289 (88), 276 (28), 264 (18), 249 (50), 235 (18), 233 (18), 213 (25).

(23R, 24S)-3β-Acetoxy-23, 24-methylenecholest-5-ene (**22**). Transformation of the i-methyl ether **7** into the anticipated acetate was accomplished by using zinc acetate in acetic acid [25]. Usual workup and recrystallization from hot methanol yielded 90% of analytically pure **22**; m.p. 165–166° (MeOH); HPLC.: t_R 126 min. – ^{1}H-NMR.: 5.38 (*m*, 1H, H–C(6)); 4.60 (*m*, 1H, H_α–C(3)); 2.033 (*s*, 3H, $COCH_3$); 1.020 (*s*, 3H, $H_3C(19)$); 1.011 (*d*, *J* = 6.48, 3H) and 0.986 (*d*, *J* = 6.22, 3H, $H_3C(26)$ and $H_3C(27)$); 0.948 (*d*, *J* = 6.19, 3H, $H_3C(21)$); 0.694 (*s*, 3H, $H_3C(18)$); 0.55 (*d*×*d*×*d*, *J* = 5, 8.5 and 8.5, 1H, H–C(28)); 0.44 (*d*×*d*×*d*×*d*, *J* = 5.5, 8.5, 8.5 and 8.5, 1H, H–C(24)); −0.33 (*d*×*d*×*d*, *J* = 5, 5 and 5, 1H, H–C(28)). – HRMS.: 440 (not detectable, M^+); 380.3440 (100, $M-HOAc$, Calc. for $C_{28}H_{44}$ 380.3443); 365.3207 (6, $C_{27}H_{41}$, $380-CH_3$); 324.2819 (4, $C_{24}H_{36}$, $380-C_4H_8$); 310.2633 (2, $C_{23}H_{34}$, $380-C_5H_{10}$); 283.2438 (3, $C_{21}H_{31}$); 259.2416 (3, $C_{19}H_{31}$); 255.2102 (6, $C_{19}H_{27}$); 253.1947 (6, $C_{19}H_{25}$); 213.1651 (5, $C_{16}H_{21}$).

Reaction of *22* with HCl in acetic acid. – The acetate **22** (40.0 mg, 0.09 mmol) was treated in the usual way. Separation of the reaction mixture by HPLC. gave 5 fractions (**23**–**27**) in a ratio 42:9:15:23:11, whereby the isolated yield of the main product **23** (fraction 1) was 41%.

Fraction 1 (*(22E, 24S)-3β-Crinosteryl acetate*, **23**). M.p. 148–150° (MeOH); HPLC.: t_R 112 min. – ^{1}H-NMR.: 5.375 (*m*, 1H, H–C(6)); 5.160 (*m*, 2H, H–C(22) and H–C(23)); 4.601 (*m*, 1H, H_α–C(3)); 2.033 (*s*, 3H, $COCH_3$); 1.019 (*s*, 3H, $H_3C(19)$); 1.002 (*d*, *J* = 6.68, 3H, $H_3C(21)$); 0.909 (*d*, *J* = 6.78, 3H, $H_3C(28)$); 0.835 (*d*, *J* = 6.52, 3H) and 0.817 (*d*, *J* = 6.63, 3H, $H_3C(26)$ and $H_3C(27)$); 0.690 (*s*, $H_3C(18)$). – HRMS.: 440 (not detectable, M^+); 380.3420 (100, $M-HOAc$, Calc. for $C_{28}H_{44}$ 380.3443); 365.3189 (5, $C_{27}H_{41}$, $380-CH_3$); 337.2897 (4, $C_{25}H_{37}$, $380-C_3H_7$); 295.2459 (1, $C_{22}H_{31}$); 282.2334 (5, $C_{21}H_{30}$); 272.2532 (2, $C_{20}H_{32}$); 267.2118 (1, $C_{20}H_{27}$); 259.2447 (2, $C_{19}H_{31}$); 255.2126 (27, $C_{19}H_{27}$); 253.1972 (6, $C_{19}H_{25}$); 228.1883 (5, $C_{17}H_{24}$); 213.1646 (5, $C_{16}H_{21}$); 201.1630 (2, $C_{15}H_{21}$).

Fraction 2 (**24**). M.p. 134–138° (MeOH); HPLC.: t_R 99 min. – MS.: 476 (not detectable, M^+), 416 (100, $M-HOAc$), 401 (12, $416-CH_3$), 380 (18, $416-HCl$), 365 (2, $416-CH_3-HCl$), 308 (16), 295 (14), 283 (10), 267 (2), 259 (10), 255 (36), 241 (3), 239 (2), 228 (8), 213 (27), 201 (6).

Fraction 3 (**25**). M.p. 123–125° (MeOH); HPLC.: t_R 95 min. – MS.: 476 (not detectable, M^+); 416 (100, $M-HOAc$), 401 (10, $416-CH_3$), 380 (80, $416-HCl$), 365 (6, $416-CH_3-HCl$), 308 (15), 296 (45), 283 (25), 281 (18), 267 (5), 259 (15), 255 (50), 253 (47), 241 (3), 239 (3), 213 (45), 201 (15).

Fraction 4 (**26**). M.p. 122–124° (MeOH); HPLC.: t_R 86 min. – MS.: 476 (4, M^+), 416 (60, $M-HOAc$), 401 (4, $416-CH_3$), 380 (100, $416-HCl$), 365 (10, $416-CH_3-HCl$), 349 (8), 337 (10), 313 (11), 308 (15), 295 (15), 282 (20), 267 (10), 255 (98), 253 (40), 241 (6), 239 (5), 228 (18), 213 (50), 201 (15).

Fraction 5 (*(23S, 24S)-3β, 23-Diacetoxy-24-methylcholest-5-ene*, **27**). HPLC.: t_R 49 min. – ^{1}H-NMR.: 5.38 (*m*, 1H, H–C(6)); 5.14 (*m*, 1H, H–C(23)); 4.60 (*m*, 1H, H_α–C(3)); 2.031 (*s*, 3H) and 2.006 (*s*, 3H, $2\,COCH_3$); 1.017 (*s*, 3H, $H_3C(19)$); 0.983 (*d*, *J* = 6.35, 3H, $H_3C(21)$); 0.906 (*d*, *J* = 7, 3H, $H_3C(28)$); 0.885 (*d*, *J* = 7, 3H) and 0.881 (*d*, *J* = 7, 3H, $H_3C(26)$ and $H_3C(27)$); 0.681 (*s*, 3H, $H_3C(18)$). – MS.: 500 (not detectable, M^+), 440 (100, $M-HOAc$), 425 (1, $440-CH_3$), 380 (15, $M-2\,HOAc$), 365 (10, $380-CH_3$), 337 (1), 326 (5), 309 (2), 296 (3), 282 (12), 272 (10), 267 (7), 259 (15), 255 (18), 253 (30), 228 (15), 213 (25), 211 (12), 201 (10).

(23S, 24R)-3β-Acetoxy-23, 24-methylenecholest-5-ene (**28**). The i-methyl ether protecting group was converted into the 3β-acetoxy-Δ^5 system as mentioned above (**7**→**22**). Usual workup and recrystallization from hot methanol yielded 76% of analytical pure **28**; m.p. 130–132° (MeOH). – ^{1}H-NMR.: 5.38 (*m*, 1H, H–C(6)); 4.60 (*m*, 1H, H_α–C(3)); 2.031 (*s*, 3H, $COCH_3$); 1.037 (*d*, *J* = 6.55, 3H) and

0.988 (*d*, J=5.10, 3 H, $H_3C(26)$ and $H_3C(27)$); 1.020 (*s*, 3 H, $H_3C(19)$); 0.975 (*d*, J=5.93, 3 H, $H_3C(21)$); 0.80 (*m*, 1 H, H–C(23)); 0.693 (*s*, 3 H, $H_3C(18)$); *ca.* 0.61 (*d*×*d*×*d*, 1 H, H–C(28)); 0.36 (*d*×*d*×*d*×*d*, J=5.5, 8.5, 8.5 and 8.5, 1 H, H–C(24)); −0.26 (*d*×*d*×*d*, J=5, 5 and 5, 1 H, H–C(28)). – HRMS.: 440 (not detectable, M^+); 380.3453 (100, M – HOAc, Calc. for $C_{28}H_{44}$ 380.3443); 365.3274 (6, $C_{27}H_{41}$, 380 – CH_3); 324.2814 (4, $C_{24}H_{36}$, 380 – C_4H_8); 310.2641 (2, $C_{23}H_{34}$, 380 – C_5H_{10}); 283.2426 (3, $C_{21}H_{31}$); 259.2420 (3, $C_{19}H_{31}$); 255.2143 (5, $C_{19}H_{27}$); 253.1965 (7, $C_{19}H_{25}$); 213.1642 (6, $C_{16}H_{21}$).

Reaction of *28* with HCl in acetic acid. – Treatment of the acetate **28** (20.0 mg, 0.045 mmol) in the usual way and separation of the mixture by HPLC. gave 6 fractions (**29**–**34**) in a ratio 25:7:13:15:17:23. The two products with olefinic side chains (fractions 1 and 2) together amounted to 30%.

*Fraction 1 ((22*E*,24*R*)-3β-Brassicasteryl acetate*, **29**). M.p. 152–154° (MeOH); HPLC.: t_R 118 min. – ^{1}H-NMR.: 5.372 (*m*, 1 H, H–C(6)); 5.181 (*m*, 2 H, H–C(22) and H–C(23)); 4.60 (*m*, 1 H, H–C(3)); 2.032 (*s*, 3 H, $COCH_3$); 1.020 (*s*, 3 H, $H_3C(19)$); 1.011 (*d*, J=6.49, 3 H, $H_3C(21)$); 0.910 (*d*, J=6.80, 3 H, $H_3C(28)$); 0.834 (*d*, J=6.5, 3 H) and 0.818 (*d*, J=6.5, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.690 (*s*, 3 H, $H_3C(18)$). – HRMS.: 440 (not detectable, M^+); 380.3452 (100, M – HOAc, Calc. for $C_{28}H_{44}$ 380.3443); 365.3156 (6, $C_{27}H_{41}$, 380 – CH_3); 337.2893 (3, $C_{25}H_{37}$, 380 – C_3H_7); 295.2420 (1, $C_{22}H_{31}$); 282.2357 (6, $C_{21}H_{30}$); 272.2499 (2, $C_{20}H_{32}$); 267.2117 (1, $C_{20}H_{27}$); 259.2438 (2, $C_{19}H_{31}$), 255.2111 (28, $C_{19}H_{37}$); 253.1946 (7, $C_{19}H_{25}$), 228.1883 (5, $C_{17}H_{24}$); 213.1652 (6, $C_{16}H_{21}$); 201.1627 (3, $C_{15}H_{21}$).

*Fraction 2 ((22*E*)-3β-Acetoxy-23-homocholesta-5,22-diene*, **30**). M.p. 148–150° (MeOH); HPLC.: t_R 113 min. – ^{1}H-NMR.: 5.372 (*m*, 1 H, H–C(6)); 5.249 (*m*, 2 H, H–C(22) and H–C(23)); 2.032 (*s*, 3 H, $COCH_3$); 1.019 (*s*, 3 H, $H_3C(19)$); 0.999 (*d*, J=6.63, 3 H, $H_3C(21)$); 0.866 (*d*, J=6.64, 3 H) and 0.862 (*d*, J=6.64, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.686 (*s*, 3 H, $H_3C(18)$). – HRMS.: 440 (not detectable, M^+); 380.3454 (100, M – HOAc, Calc. for $C_{28}H_{44}$ 380.3443); 365.3211 (7, $C_{27}H_{41}$, 380 – CH_3), 295.2450 (1, $C_{22}H_{31}$); 282.2327 (8, $C_{21}H_{30}$); 267.2113 (3, $C_{20}H_{27}$); 259.2421 (4, $C_{19}H_{31}$); 255.2111 (26, $C_{19}H_{37}$); 253.1944 (7, $C_{19}H_{25}$); 228.1872 (3, $C_{17}H_{24}$); 213.1642 (6, $C_{16}H_{21}$); 201.1639 (2, $C_{15}H_{21}$).

Fraction 3 (**31**). M.p. 140° (MeOH); HPLC.: t_R 104 min. – MS.: 476 (not detectable, M^+), 416 (100, M – HOAc), 401 (10, 416 – CH_3), 380 (60, 416 – HCl), 365 (5, 416 – CH_3 – HCl), 308 (15), 296 (15), 283 (15), 259 (13), 255 (40), 253 (27), 213 (30), 201 (8).

Fraction 4 (**32**). M.p. 110° (MeOH); HPLC.: t_R 97 min. – MS.: 476 (not detectable, M^+), 416 (50, M – HOAc), 401 (5, 416 – CH_3), 380 (100, 416 – HCl), 365 (9, 416 – CH_3 – HCl), 308 (8), 296 (30), 283 (27), 267 (6), 259 (9), 255 (51), 253 (43), 239 (6), 228 (15), 213 (37), 201 (13).

Fraction 5 (**33**). M.p. 135 – 140° (MeOH); HPLC.: t_R 93 min. – MS.: 476 (not detectable, M^+), 416 (30, M – HOAc), 401 (4, 416 – CH_3), 380 (100, 416 – HCl), 365 (10, 416 – CH_3 – HCl), 308 (6), 295 (10), 283 (14), 267 (6), 259 (9), 255 (60), 253 (28), 239 (4), 228 (12), 213 (28), 201 (10).

*Fraction 6 ((23*R*,24*R*)-3β,23-Diacetoxy-24-methylcholest-5-ene*, **34**). HPLC.: t_R 51 min. – ^{1}H-NMR.: 5.38 (*m*, 1 H, H–C(6)); 5.09 (*m*, 1 H, H–C(23)); 4.60 (*m*, 1 H, H_a–C(23)); 2.038 (*s*, 3 H) and 2.032 (*s*, 3 H, 2 $COCH_3$); 1.016 (*s*, 3 H, $H_3C(19)$); 0.957 (*d*, J=6.39, 3 H, $H_3C(21)$); 0.929 (*d*, J=6.78, 3 H, $H_3C(28)$); 0.821 (*d*, J=6.75, 3 H) and 0.813 (*d*, J=6.91, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.660 (*s*, 3 H, $H_3C(18)$). – MS.: 500 (not detectable, M^+), 440 (100, M – HOAc), 380 (30, M – 2 HOAc), 365 (15, 380 – CH_3), 326 (3), 296 (5), 282 (20), 272 (12), 259 (23), 255 (35), 253 (65), 239 (8), 228 (15), 213 (40), 201 (15).

*(22*E,*24*S*)-Crinosterol* (**4**). The 3β-hydroxy-Δ^5 system was regenerated from **23** in the usual manner to give the crystalline sterol **4**, m.p. 152–154° (MeOH). – ^{1}H-NMR.: 5.349 (*m*, 1 H, H–C(6)); 5.162 (*m*, 2 H, H–C(22) and H–C(23)); 3.53 (*m*, 1 H, H_a–C(3)); 1.010 (*s*, 3 H, $H_3C(19)$); 1.001 (*d*, J=6.20, 3 H, $H_3C(21)$); 0.910 (*d*, J=6.86, 3 H, $H_3C(28)$); 0.836 (*d*, J=6.45, 3 H) and 0.817 (*d*, J=6.62, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.693 (*s*, 3 H, $H_3C(18)$). – HRMS.: 398.3551 (100, M^+, Calc. for $C_{28}H_{46}O$ 398.3549); 383.3325 (8, $C_{27}H_{43}O$, M – CH_3); 380.3451 (15, $C_{28}H_{44}$, M – H_2O); 365.3217 (9, $C_{27}H_{41}$, M – CH_3 – H_2O); 355.3037 (5, $C_{25}H_{39}O$, M – C_3H_7); 337.2917 (11, $C_{25}H_{37}$, M – C_3H_7 – H_2O); 313.2918 (5, $C_{23}H_{37}$); 300.2457 (40, $C_{21}H_{32}O$); 299.2380 (7, $C_{21}H_{31}O$); 285.2210 (8, $C_{20}H_{29}O$); 282.2330 (6, $C_{21}H_{30}$); 273.2204 (15, $C_{19}H_{29}O$); 271.2059 (40, $C_{19}H_{27}O$); 267.2133 (6, $C_{20}H_{27}$); 255.2124 (44, $C_{19}H_{27}$); 241.1946 (5, $C_{18}H_{25}$); 229.1595 (4, $C_{16}H_{21}O$); 213.1638 (11, $C_{16}H_{21}$); 201.1661 (4, $C_{15}H_{21}$).

*(22*E,*24*R*)-Brassicasterol* (**6**). Cleavage of the acetoxy group in **29** as usual gave the desired free sterol **6**; m.p. 156–158° (MeOH); HPLC. (ODS-2): t_R 55 min. – ^{1}H-NMR.: 5.348 (*m*, 1 H, H–C(6)); 5.181 (*m*, 2 H, H–C(22) and H–C(23)); 3.53 (*m*, 1 H, H_a–C(3)); 1.011 (*d*, J=6.34, 3 H, $H_3C(21)$);

1.010 (*s*, 3 H, $H_3C(19)$); 0.910 (*d*, $J = 6.84$, 3 H, $H_3C(28)$); 0.834 (*d*, $J = 6.10$, 3 H) and 0.817 (*d*, $J = 6.22$, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.693 (*s*, 3 H, $H_3C(18)$). – HRMS.: 398.3545 (100, M^+, Calc. for $C_{28}H_{46}O$ 398.3549); 383.3328 (7, $C_{27}H_{43}O$, $M-CH_3$); 380.3469 (11, $C_{28}H_{44}$, $M-H_2O$); 365.3234 (8, $C_{27}H_{41}$, $M-CH_3-H_2O$); 355.2961 (7, $C_{25}H_{39}O$, $M-C_3H_7$); 337.2919 (9, $C_{25}H_{37}$, $M-C_3H_7-H_2O$); 313.2882 (6, $C_{23}H_{37}$); 300.2454 (42, $C_{21}H_{32}O$); 299.2389 (7, $C_{21}H_{31}O$); 285.2216 (7, $C_{20}H_{29}O$); 283.2436 (8, $C_{21}H_{31}$); 271.2057 (34, $C_{19}H_{27}O$); 267.2071 (6, $C_{20}H_{27}$); 255.2100 (35, $C_{19}H_{27}$); 231.1740 (5, $C_{16}H_{23}O$); 227.1800 (6, $C_{17}H_{23}$); 213.1637 (13, $C_{16}H_{21}$); 201.1623 (3, $C_{15}H_{21}$).

(22E)-23-Homocholesta-5,22-dien-3β-ol (**35**). Regeneration of the 3β-hydroxy-Δ^5-system from the acetate **30** yielded the desired free sterol **35**; HPLC. (ODS-2): t_R 49 min. – ^{1}H-NMR.: 5.349 (*m*, 1 H, H–C(6)); 5.249 (*m*, 2 H, H–C(22) and H–C(23)); 3.53 (*m*, 1 H, H_α–C(3)); 1.009 (*s*, 3 H, $H_3C(19)$); 0.999 (*d*, $J = 6.46$, 3 H, $H_3C(21)$); 0.866 (*d*, $J = 6.47$, 3 H) and 0.863 (*d*, $J = 6.75$, 3 H, $H_3C(26)$ and $H_3C(27)$); 0.689 (*s*, 3 H, $H_3C(18)$). – HRMS.: 398.3520 (100, M^+, Calc. for $C_{28}H_{46}O$ 398.3549); 383.3289 (12, $C_{27}H_{43}O$, $M-CH_3$); 380.3405 ($C_{28}H_{44}$, $M-H_2O$); 365.3191 (10, $C_{27}H_{41}$, $M-CH_3-H_2O$); 300.2450 (69, $C_{21}H_{32}O$); 287.2726 (9, $C_{21}H_{35}$); 285.2215 (17, $C_{20}H_{29}O$); 282.2331 (6, $C_{21}H_{30}$); 273.2199 (21, $C_{19}H_{29}O$); 271.2064 (42, $C_{19}H_{27}O$); 267.2091 (9, $C_{20}H_{27}$); 258.1967 (10, $C_{18}H_{26}O$); 255.2109 (54, $C_{19}H_{27}$); 253.1970 (10, $C_{19}H_{25}$); 241.1954 (8, $C_{18}H_{25}$); 239.1795 (7, $C_{18}H_{23}$); 228.1866 (5, $C_{17}H_{24}$); 215.1812 (9, $C_{16}H_{23}$); 213.1646 (17, $C_{16}H_{21}$); 201.1635 (5, $C_{15}H_{21}$).

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