XyMTEX (Version 4.04) for Typesetting Chemical Structural Formulas. An Extension for Drawing Steroid Derivatives.

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Contents

Chapter 1

Introduction

1.1 History

The history of the XyMTeX system is summarized in Table 1.1:

Table 1.1: Versions of XyMTeX

version	package files and comments
1.00 (1993)	(for LaTeX2.09) See Ref. [1, 2]. aliphat.sty, carom.sty, lowcycle.sty, hetarom.sty, hetaromh.sty, hcycle.sty, chemstr.sty, locant.sty, xymtex.sty
1.01 (1996)	(for LaTeX 2_ε) See Ref. [3]. ccycle.sty, polymers.sty, chemist.sty
1.02 (1998)	(not released) Nested substitution by 'yl'-function.
2.00 (1998)	Enhanced version based on the XyM Notation. See Ref. [4, 5]. fusering.sty, methylen.sty
2.01 (2001)	(not released) Size reduction, sizeredc.sty (version 1.00)
3.00 (2002)	Size reduction (sizeredc.sty, version 1.01), and reconstruction of the command system. See Ref. [6]
4.00 (2002)	(not released) PostScript printing (xymtx-ps.sty, version 1.00 and chmst-ps.sty, version 1.00)
4.01 (2004)	PostScript printing and length-variable central atoms
4.02 (2004)	PostScript printing and wedges bonds for stereochemistry
4.03 (2005)	PostScript printing and wavy bonds for stereochemistry
4.04 (2009)	(this version) Macros for drawing steroids (steroid.sty, ver 1.00)

1. **PostScript Compatibility**: XyMTeX after version 4.00 provides us with functions for supporting PostScript, where PSTrick [8] is used to generate PostScript codes embedded in a DVI (device-independent) file, as described in the manual for XyMTeX Version 4.01 [7]. After converting the DVI file into a PostScript file by such a converter as dvips, the PostScript file containing XyMTeX structural formulas can be processed by PostScript printer drivers or by the GhostScript interpreter so as to produce printed documents [9]. As a result, the XyMTeX system is now free from the limitations of the LaTeX picture environment. Although the enhanced flexibility of XyMTeX has been accomplished at the expense of portability within TeX/LaTeX, it assures a further expansion of the domain of XyMTeX, where various functions due to PostScript can be used to draw structural formulas.

2. **Functions for Stereochemistry**: One of the most important features of XyMTEX version 4.02 is that new stereochemical functions are supported, where a pair of wedged bonds/hashed dash bonds, a pair of wedged bonds/hashed wedged bonds, and a pair of dash bonds/hashed dash bonds can be switched to draw structural formulas with specified absolute configurations.

3. **Steroid Derivatives**: The present version (XyMTEX version 4.04) supports devices for drawing steroid derivatives, which employ stereochemical functions of the versions after 4.00.

4. **Compatibility with the LaTeX Picture Environment**: The previous mode using the LaTeX picture environment is also available, although several stereochemical expressions are replaced by alternative ones within the environment.

1.2 Package Files of XyMTEX Version 4.04

The XyMTEX system (version 4.04) consists of the package files listed in Table 1.2, where the package steroid.sty has been developed to draw steroid derivatives. Trivial and systematic names of steroids and their structural formulas are taken from the reports on IUPAC nomenclatures [10, 11].

Table 1.2: Package Files of XyMTEX and Related Files

package name	included functions
XyMTEX Files	
aliphat.sty	macros for drawing aliphatic compounds
carom.sty	macros for drawing vertical and horizontal types of carbocyclic compounds
lowcycle.sty	macros for drawing five-or-less-membered carbocycles.
ccycle.sty	macros for drawing bicyclic compounds etc.
hetarom.sty	macros for drawing vertical types of heterocyclic compounds
hetaromh.sty	macros for drawing horizontal types of heterocyclic compounds
hcycle.sty	macros for drawing pyranose and furanose derivatives
chemstr.sty	basic commands for atom- and bond-typesetting
locant.sty	commands for printing locant numbers
polymers.sty	commands for drawing polymers
fusering.sty	commands for drawing units for ring fusion
methylen.sty	commands for drawing zigzag polymethylene chains
sizeredc.sty	commands for size reduction
xymtx-ps.sty	macros for PostScript printing (XyMTEX Version 4.02). These macros are substituted for several macros contained in the chemstr package.
steroid.sty	macros for drawing steroid derivatives contained in the steroid package (XyMTEX Version 4.04)
XyMTEX Utilities	
xymtex.sty	a package for calling all package files except xymtx-ps.sty (no PostScript)
xymtexps.sty	a package for calling all package files (PostScript, i.e. with xymtx-ps.sty)
Related Files	
chemist.sty	commands for using 'chem' version and chemical environments
chmst-ps.sty	macros for PostScript printing. These macros are substituted for several macros contained in chemist package.

XyMTEX Version 4.04 works in two modes:

1. TEX/LATEX compatible mode: When xymtex.sty is input, all of the package files of the XYMTEX system except xymtx-ps.sty are loaded. This mode draws β-bonds as thick lines and α-bonds as dotted lines.

```
¥documentclass{article}
¥usepackage{xymtex}
¥begin{document}
(formula)
¥end{document}
```

   To reduce formula sizes, epic.sty is automatically loaded.

2. PostScript compatible mode: When xymtexps.sty is input, all of the package files of the XYMTEX system (also xymtx-ps.sty) are loaded. This mode draws β/α-bonds in one format selected from a pair of wedged bonds/hashed dash bonds (default), a pair of wedged bonds/hashed wedged bonds, and a pair of dash bonds/hashed dash bonds.

```
¥documentclass{article}
¥usepackage{xymtexps}
¥begin{document}
(formula)
¥end{document}
```

After compiling these TEX files by the TEX system, the resulting DVI files are converted in the PostScript files, which are printed by PostScript tools.

Chapter 2

Basic Skeletons for Drawing Steroids

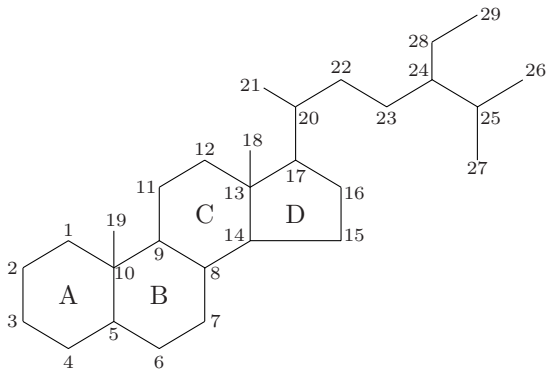
2.1 Macros for Drawing Basic Skeletons

In addition to the macros `¥steroid` and `¥stereochain` defined previously, several basic macros for drawing steroid derivative have been defined (Table 2.1). Each of these macros is capable of accommodating substituents in a main argument (SUBSLIST) and bond descriptors in an optional argument (BONDLIST):

```
¥Sforma[BONDLIST]{SUBSLIST}
```

where `¥Sforma` represents an appropriate command name. Modes of substitution are specified by using the main argument and the optional one according to conventions of locant numbering for steroid derivatives, as described in Section 5.3 of the online manual of XyMTEX Version 1.00 (xymtex.pdf).

The carbon atoms of a steroid skeleton with a 17-side chain are numbered sequentially and the four rings are designated by alphabets A–D.



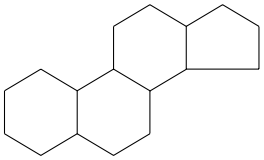
2.2 Basic Derivations

2.2.1 Substitutions

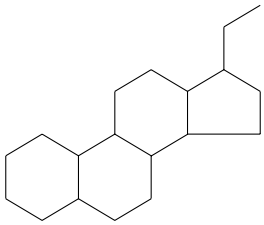
In the pregnane series, the stereochemistry at C-20 was formerly designated by the so-called $20\alpha/20\beta$ convention, which is now discouraged in favor of the CIP (Cahn-Ingold-Prelog) priority system.

In the process of applying the $20\alpha/20\beta$ convention, the side chain of a pregnane skeleton is placed in agreement with a Fischer projection. Such a Fischer projection can be depicted by an equivalent expression using wedged and bold dashed bonds. To exemplify a 20α substituent, the following formula is depicted by nesting the `¥tetrahedral` command in the `¥steroid` command, where a (yl) function of XyMTEX is used.

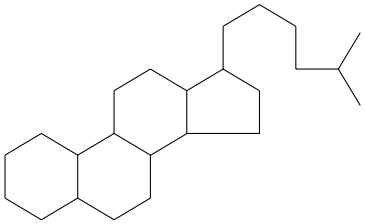
Table 2.1: Basic Skeletons for Drawing Steroids



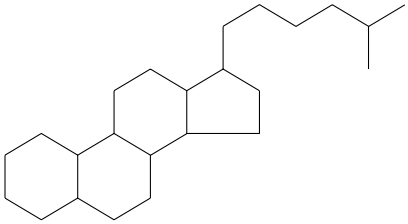
¥steroid{}



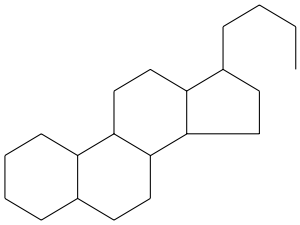
¥steroidethylchain{}



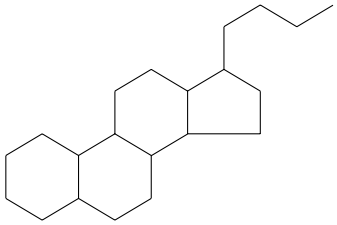
¥steroidchain{}



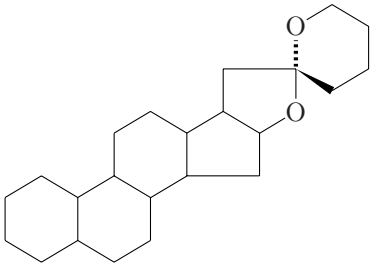
¥steroidChain{}



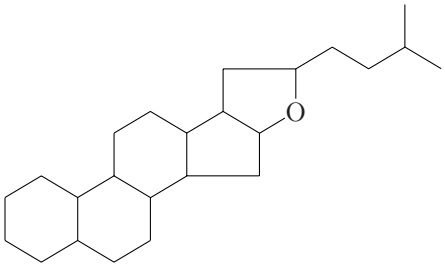
¥steroidshortchain{}



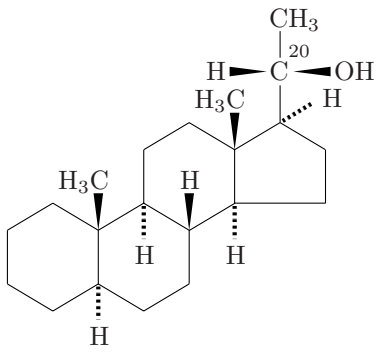
¥steroidShortChain{}



¥steroidspiro



¥steroidfuros{}

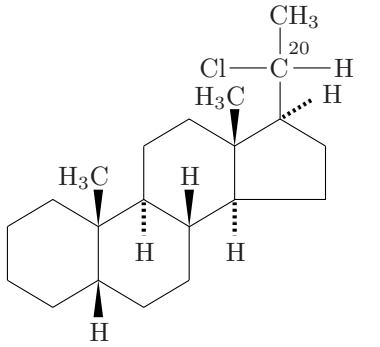


5α-pregnan-20α-ol (formerly)
(20S)-5α-pregnan-20-ol

```
¥begin{XyMcompd}(1200,1250)(300,150){}{}
¥steroid{5A==H;%
{10}B==¥lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==¥lmoiety{H$_{3}$C};
{17}==¥tetrahedral{3==(yl);%
0==C¥rlap{¥raisebox{5pt}{$^{20}$}};%
2B==H;4B==OH;1==CH$_{3}$};%
{17}GA==H}
¥end{XyMcompd}
```

In the above program, the `XyMcompd` environment of the chemist package is used in order to secure an adequate drawing area (the argument `(1200,1250)`) for accommodating the formula to be drawn. The second argument `(300,150)` indicates the x- and y shift values applied to the drawing area.

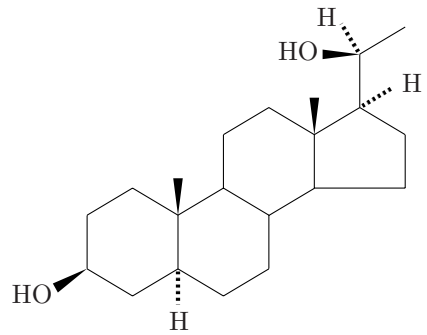
For the purpose of the strict adoption of a Fischer projection, the code `2B==H;4B==OH;` should be replaced by the code `2==H;4==OH;` in the main argument of the inner `¥tetrahedral` command. To exemplify a 20β substituent in this way, the following formula is depicted:



20β-chloro-5β-pregnane (formerly)
(20R)-20-chloro-5β-pregnane

```
¥begin{XyMcompd}(1200,1250)(300,150){}{}
¥steroid{5B==H;%
{10}B==¥lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==¥lmoiety{H$_{3}$C};
{17}==¥tetrahedral{3==(yl);%
0==C¥rlap{¥raisebox{5pt}{$^{20}$}};%
2==Cl;4==H;1==CH$_{3}$};%
{17}GA==H}
¥end{XyMcompd}
```

Even for the purpose of naming pregnane series, the CIP priority system is now preferred to designate the stereochemistry at C-20, where a Fischer projection is no longer necessary. Moreover, methyl substituents at C-10 and C-13 are frequently expressed by wedged bonds without the explicit specification of CH_3; and hydrogens at C-8, C-9, and C-14 along with their incident bonds are sometimes omitted. However, a hydrogen at C-5 is always designated by a wedged bond (5β) or a bold dashed bond (5α) (with the specification of the atom H), because the configuration at C-5 is not contained in the name of the basic skeleton *pregnane*.



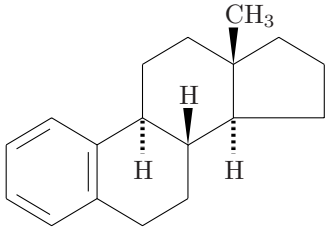
(20S)-5α-pregnan-3β,20-diol

```
¥begin{XyMcompd}(1400,1200)(0,150){}{}
¥steroidethylchain{5A==H;3B==HO;%
{10}B==¥null;{13}B==¥null;%
{20}Su==HO;{20}Sd==H;{17}GA==H}
¥end{XyMcompd}
```

2.2.2 Unsaturation

To specify double bonds in a steroid skeleton, the optional argument (bondlist) of each command is used. For example, estra-1,3,5(10)-triene is depicted by using the `¥steroid` command with the optional argument `[ack]`, where the alphabet `a` denotes the unsaturation between C-1 and C-2, the alphabet `c`

denotes the unsaturation between C-3 and C-4, and the alphabet `k` denotes the unsaturation between C-5 and C-10.

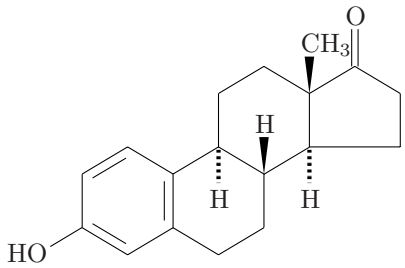


estra-1,3,5(10)-triene

```
¥steroid[ack]{8B==H;9A==H;{13}B==CH$_{3}$;%
{14}A==H}
```

Strictly speaking, another set of double bonds can be selected, i.e., 1(10),2,4, to show the aromatization of ring A. We tentatively select 1,3,5(10) by considering that the sequence of locant numbers (containing implicit ones such as 1(2) and 3(4)) is not disturbed as far as possible.

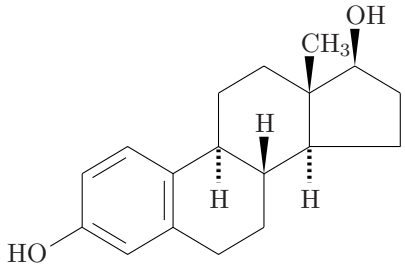
Estrone was isolated from the urine of pregnant women as the first isolated one of estrogens (female sex hormones). The structural formula of estrone is drawn by using the command `¥steroid`.



3-hydroxyestra-1,3,5(10)-trien-17-one
estrone

```
¥steroid[ack]{3==HO;{17}D==O;%
8B==H;9A==H;{13}B==CH$_{3}$;{14}A==H}
```

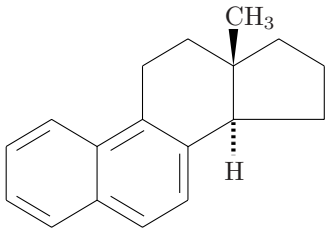
Estradiol, which is a much more potent estrogen than estrone, is drawn by using the command `¥steroid` as follows:



estra-1,3,5(10)-triene-3,17β-diol
estradiol

```
¥steroid[ack]{3==HO;{17}B==OH;%
8B==H;9A==H;{13}B==CH$_{3}$;{14}A==H}
```

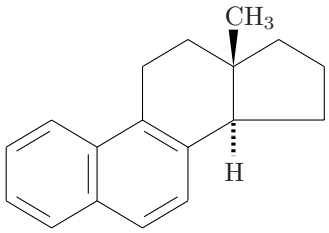
If there is a choice of locants, single ones (e.g., 5,7,9 for the aromatization of ring B) are preferred to compound locants (e.g., 5(10),6,8). For example, the following set of locants generated by the argument `[acegi]`:



estra-1,3,5,7,9-pentaene (preferred)

```
¥steroid[acegi]{{13}B==CH$_{3}$;{14}A==H}
```

is preferred to an alternative set of locants for aromatization:

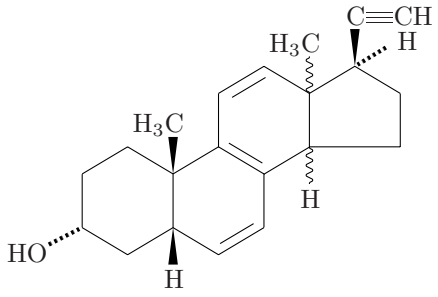


estra-1,3,5(10),6,8-pentaene (not preferred)

```
¥steroid[acfHk]{{13}B==CH$_{3}$;{14}A==H}
```

which is generated by the argument `[acfHk]`. Note that the bond indicator `H` puts a double bond inside ring B, while the lowercase indicator `h` puts a double bond inside ring C. On a similar line, the selection of a further set of locants 1(10),2,4,6,8 in not preferred.

The following example illustrates a method for drawing double bonds, where the lowercase indicator `h` in place of the uppercase one puts a double bond inside ring C. It shows also a method for drawing substituents with an undetermined configuration (ξ-bond), where the alphabet `U` in the descriptor `{14}U==H` means an undetermined configuration:

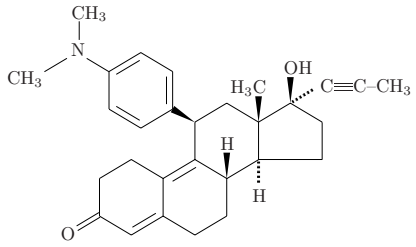


5β,13ξ,14ξ-pregna-6,8,11-trien-20-yn-3α-ol

```
¥steroid[fhm]{3A==HO;5B==H;%
{10}B==¥lmoiety{H$_{3}$C};%
{13}U==¥lmoiety{H$_{3}$C};{14}U==H;%
{17}B=={C¥triplebond CH};{17}GA==H}
```

Note that the command `¥triplebond` has been defined in the chemist package. The command `¥lmoiety` is used to draw a leftward substituent at a site having an implicit rightward substituent.

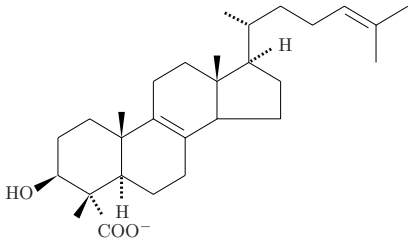
The formula of mifepristone (RU-486), which is a synthetic steroid used as a abortifacient in the first two month of pregnancy, is drawn by using the command `stereoid`.



11β-[4-(dimethylamino)phenyl]-17β-hydroxy-
17α-(1-propynyl)estra-4,9-dien-3-one
(RU-486, mifepristone)

```
¥begin{XyMcompd}(2000,1300)(-200,200){}{}
¥steroid[di]{3D==O;8B==H;%
{11}B==¥bzdrv{3==(yl);%
6==¥Dtrigonal{0==N;1==CH$_{3}$;%
3==CH$_{3}$;2==(yl)}};%
{13}B==¥lmoiety{H$_{3}$C};{14}A==H;%
{17}GA=={C¥triplebond C--CH$_{3}$};{17}B==OH}
¥end{XyMcompd}
```

Other commands for drawing steroid skeletons (Table 2.1) are also capable of putting double bonds by using their bondlists, which are prepared as optional arguments. The following compound is drawn by using `¥steroidChain` with the descriptor `h{Ze}` in the optional argument (bondlist). A double bond in the 17-side chain is specified by an alphabet with the letter `Z` (e.g., `{Ze}`).



3β-hydroxy-4β-methyl-5α-cholesta-8,24-diene-4α-carboxylate
or 3β-hydroxy-30-norlanosta-8,24-dien-28-oate

```
¥steroidChain[h{Ze}]
{3B==HO;4SB==¥null;4SA==COO$^{-}$;
5A==H;{10}B==¥null;{13}B==¥null;%
{17}GA==H;{20}A==¥null}
```

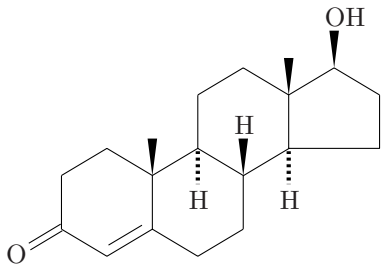
The resulting compound can be named as a derivative of cholestane or as a derivative of lanostane (one of triterpenes). The prefix 30-nor in the latter name means that the 30-methyl (at the C-14 position of the steroid numbering) is deleted from the parent name lanostane. The α- and β-methyl groups at the C-4 of the lanostane skeleton are numbered to be 28 and 29 respectively. The end -28-oate of the name stems from this convention of locant numbering.

2.3 Stereochemical Modifications

As for the systematic nomenclature for stereochemical modifications of steroids, see IUPAC-IUB (1989) 3S-5 [11].

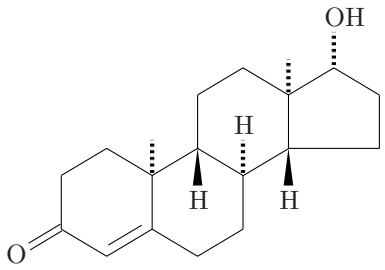
2.3.1 Enantiomers—Use of the Prefix *ent-*

When either steroid derivative of an enantiomeric pair is referred to by using a systematic name (or a trivial name), the other one (its enantiomer) is designated by using the prefix *ent-* (a contracted form of *enantio-*), which means the enantiomeric relationship between the two derivatives at issue. It should be noted that this prefix denotes inversion at all asymmetric centers whether these are cited explicitly or are implied in the name. For example, the descriptor 17β in the name of the latter derivative is in fact inverted into 17α, as found in the corresponding formula. See IUPAC-IUB (1989) 3S-5.1 [11].



17β-hydroxyandrost-4-en-3-one
(testosterone)

```
¥steroid[d]{3D==O;8B==H;9A==H;%
{10}B==¥null;%
{13}B==¥null;{14}A==H;{17}B==OH}
```

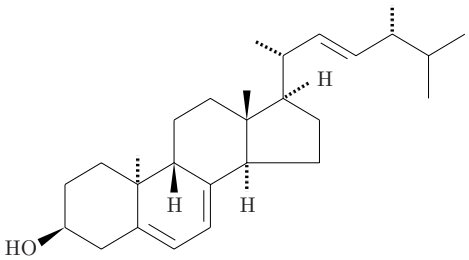


ent-17β-hydroxyandrost-4-en-3-one
(*ent*-testosterone)

```
¥steroid[d]{3D==O;8A==H;9B==H;%
{10}A==¥null;%
{13}A==¥null;{14}B==H;{17}A==OH}
```

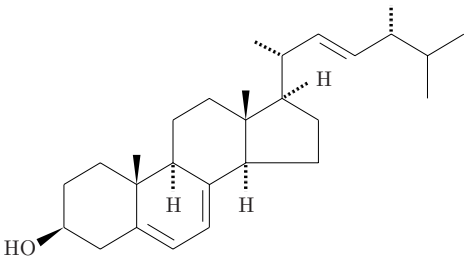
2.3.2 Use of α and β for Inverted Bridgeheads

Suppose that not more than half of the asymmetric centers whose configurations need not be specified in a name of the parent compound are inverted into opposite configurations. Then such inverted centers are specified by using α and β-descriptors. An example (lumisterol) is depicted as follows, which also exemplifies double bond specification at a side chain. Note that 9β and 10α are such inverted asymmetric centers to be specified. See IUPAC-IUB (1989) 3S-5.2 [11]. The trivial name ergosterol is used to refer to the 9α,10β-stereoisomer, which are not explicitly specified in the corresponding systematic name, because the parent name ergosterol implies the configurations of 9α,10β, which are not explicitly specified, as found in the second formula below.




```
¥steroidChain[eg{Zc}]%
{3B==HO;9B==H;{10}A==¥null;%
{13}B==¥null;{14}A==H;{17}GA==H;%
{20}A==¥null;{24}A==¥null}
```

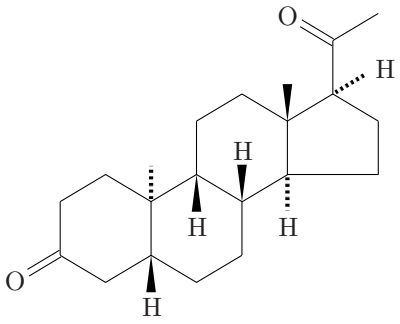
(22E)-9β,10α-ergosta-5,7,22-trien-3β-ol
(trivial name: lumisterol)




```
¥steroidChain[eg{Zc}]%
{3B==HO;9A==H;{10}B==¥null;%
{13}B==¥null;{14}A==H;{17}GA==H;%
{20}A==¥null;{24}A==¥null}
```

(22E)-ergosta-5,7,22-trien-3β-ol
(trivial name: ergosterol)

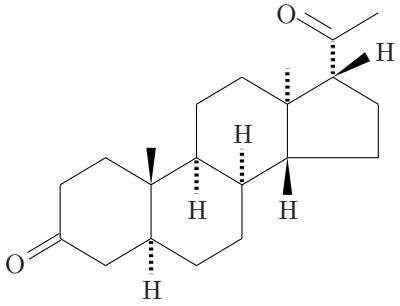
The name of the following derivative is based on 5β-pregnane-3,20-dione, whose bridgeheads (implied by 9α and 10β) are inverted into opposite configuration, as denoted by 9β and 10α. See also IUPAC-IUB (1989) 3S-5.2 [11].



5β,9β,10α-pregnane-3,20-dione

```
¥steroidethylchain{3D==O;5B==H;8B==H;%
9B==H;{10}A==¥null;{13}B==¥null;{14}A==H;%
{17}GA==H;{20}D==O}
```

The enantiomer of the above derivative is named by using the prefix *ent-*. The name based on 5α-pregnane-3,20-dione (in a pair of parentheses) is not suitable because the number of inverted centers is more than half of its asymmetric centers.

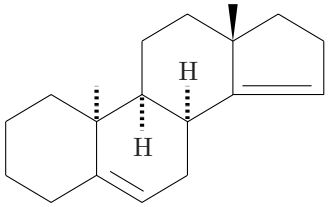


ent-5β,9β,10α-pregnane-3,20-dione
(not 5α,8α,13α,14β,17α-pregnane-3,20-dione)

```
¥steroid{3D==O;5A==H;8A==H;%
9A==H;{10}B==¥null;{13}A==¥null;{14}B==H;%
{17}GB==H;%
{17}A==¥trimethylenei[a]{1==O}{2==(yl)}}
```

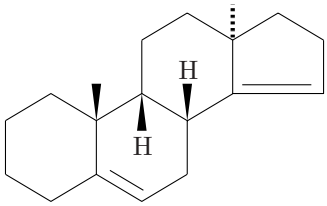
2.3.3 Selection of Starting Structures for Assigning α/β and *ent-*

Suppose that just the half of the asymmetric centers whose configurations need not be specified in a name of the parent compound are inverted into opposite configurations. The youngest sequence selected from the series 8, 9, 10, 13, 14, and 17 is adopted to decide whether the prefix *ent-* is used or not.



8α,10α-androsta-5,14-diene

```
¥steroid[eq]{8A==H;9A==H;%
{10}A==¥null;{13}B==¥null}
```



ent-8α,10α-androsta-5,14-diene
(not 9β,13α-androsta-5,14-diene)

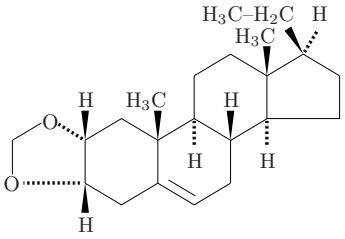
```
¥steroid[eq]{8B==H;9B==H;%
{10}B==¥null;{13}A==¥null}
```

Note that 8α,10α has preference over 9β,13α for the α/β specification of inverted bridgeheads, because 8β, 9α, 10β, and 13β are the implicit configurations of the starting steroid, i.e., androsta-5,14-diene.

2.4 Steroids with Additional Rings

2.4.1 Steroids with Fused Rings

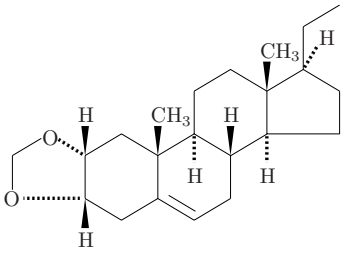
Steroid skeletons listed in Table 2.1 are capable of accommodating fused rings in their bondlist. For example, 2α,3α-dihydroxyl groups of pregn-5-ene-2α,3α-diol can form a 1,3-dioxolane ring. The resulting 1,3-dioxolane ring can be drawn by using `¥fivefusevi` in the bondlist of `¥steroid`, as shown in the following structure:



2α,3α-(methylenedioxy)pregn-5-ene

```
¥steroid[e%
{B{¥fivefusevi({aA}{cA}){1==O;4==O}{}{b}}}]%
{2GB==H;3FB==H;%
{10}B==¥lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==¥lmoiety{H$_{3}$C};
{17}SB==H$_{3}$C--H$_{2}$C;{17}SA==H}
```

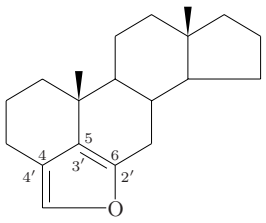
For the nomenclature, see IUPAC-IUB (1989) 3S-10.1 [11]. By using the `¥pregnane` command, a simpler program is available as follows:



2α,3α-(methylenedioxy)pregn-5-ene

```
¥pregnane[e%
{B{¥fivefusevi({aA}{cA}){1==O;4==O}{}{b}}}]%
{2GB==H;3FB==H}
```

Fusion of a furan ring component to a steroid can be named by means of a modification of fusion nomenclature. For a modification of fusion nomenclature to be applied to steroids, see IUPAC-IUB (1989) 3S-10.2 [11]. The following example exemplifies such a fusion as described by the descriptor [4′,3′,2′:4,5,6], where the former three integers indicate the fusion positions of the furan ring, while the latter three indicate those of the steroid skeleton. The latter ascending sequence (i.e., 4,5,6) of the steroid is preferred so as to result in the descending order of the former sequence (i.e., 4′,3′,2′) of the furan ring. The furan ring component is drawn by means of the `¥fivefusevi` command, which is incorporated in the optional argument (bondlist) of the `¥steroid` command.

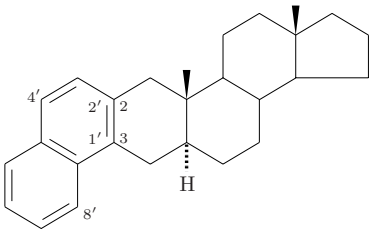


furo[4′,3′,2′:4,5,6]androstane

```
¥steroid
[{c{¥fivefusevi[ad]{3==O}{}{e}[a]}}]
{{10}B==¥null;{13}B==¥null}
```

Fusion of a naphthalene ring component to a steroid can be also named by means of a modification of fusion nomenclature. The following example exemplifies such a fusion as described by the descriptor [2′,1′:2,3], which shows that the locant numbers involved in fusion are ordered in accord with those (i.e., 2,3) of the steroid skeleton.

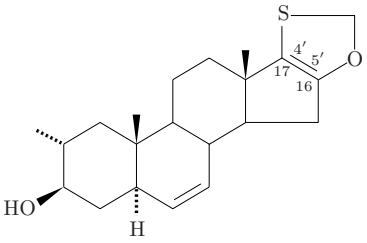
The naphthalene ring component is drawn by means of two ¥sixfusev commands, which are nested by using the optional arguments.



naphtho[2′,1′:2,3]-5α-androstane

```
¥begin{XyMcompd}(1600,1100)(-250,-50){}{}
¥steroid[{B{¥sixfusev[bdf
{D{¥sixfusev[ce]{}{}{a}}}]{}{}{b}}}]
{5A==H;{10}B==¥null;{13}B==¥null}
¥end{XyMcompd}
```

The following example shows fusion of a heterocycle (a [1,3]oxathiolo unit) to a steroid skeleton at the bond between the C-16 and the C-17. The fusion of the [1,3]oxathiolo unit is depicted by means of the ¥fivefusev command.

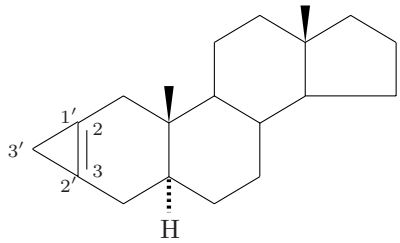


2α-methyl[1,3]oxathiolo[5′,4′:16,17]-5α-androst-6-en-3β-ol

```
¥begin{XyMcompd}(1600,1100)(0,100){}{}
¥steroid[%
f{s{¥fivefusev[e]{2==O;4==S}{}{e}}}]
{2A==¥null;3B==HO;5A==H;{10}B==¥null;{13}B==¥null}
¥end{XyMcompd}
```

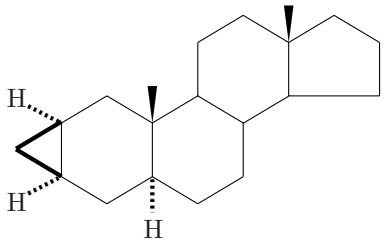
The numbering of the steroid moiety is retained and the atoms of the attached component are identified by primed locants. As found in the descriptor [5′,4′:16,17], the locant numbers involved in fusion are ordered in accord with those (i.e., 16,17) of the steroid skeleton.

The descriptor 3′*H* in the following IUPAC name is an indicated hydrogen to specify the unsaturation of a fused cyclopropene ring. The descriptor [2,3] for designating the fused position is an abbreviation of [1′,2′:2,3].



3′*H*-cyclopropa[2,3]-5α-androstane

```
¥steroid[b{b¥threefusehi{}{}{b}}]
{5A==H;{10}B==¥null;{13}B==¥null}
```

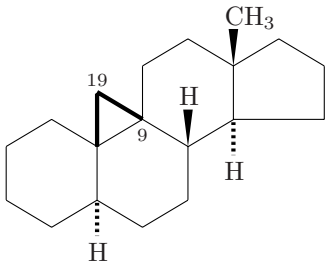


2α,3α-dihydro-3′*H*-cyclopropa[2,3]-5α-androstane

```
¥steroid
[{b¥threefusehi({aB}{cB}){}{}{b}}]
{5A==H;{10}B==¥null;{13}B==¥null;%
2A==H;3A==H}
```

2.4.2 Additional Rings Formed within the Steroid Skeleton

A cyclopropane ring fusion is exemplified by the following structure, where the ¥threefuseh command is used as an optional argument (bondlist). The bond identifier I (uppercase) is used in place of i (lowercase) to assure the correct ring fusion at a bond between 9 and 10. The designator, 9,19-cyclo, in the IUPAC nomenclature (cf. IUPAC-IUB (1989) 3S-2.10 [11]) means that the 19-methyl (at the C-10) is linked to the C-9, forming a cyclopropane ring.

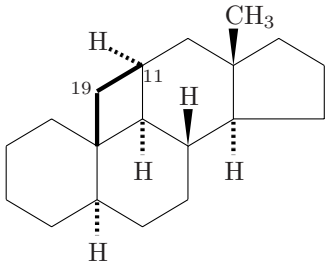


9,19-cyclo-5α,9β-androstane

```
¥steroid[{I¥threefuseh({bB}{cB}){}{}{a}}]
{5A==H;8B==H;{13}B==CH$_{3}$;{14}A==H}
```

Note that the optional arguments `({bB}{cB})` specify the boldfaced bonds of the fused cyclopropane ring. Because the 19-methyl is linked implicitly through a β-bond to the C-10 of 5α-androstane, the IUPAC name does not contain the designation of the C-10 position. On the other hand, the 5α-androstane implies a 9α-configuration so that 9β is explicitly declared in the resulting IUPAC name.

The linkage between the 19-methyl (at the C-10) and the C-11 results in the formation of a cyclobutane ring. The resulting ring is depicted by using two commands, `¥threefuseh` and `¥threefusehi`, as shown in the following example.

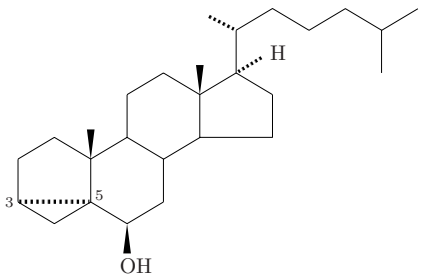


11β,19-cyclo-5α-androstane

```
¥steroid[{I¥threefuseh({bB}){}{}{a}[c]}%
{1¥threefusehi({cB}){}{}{b}[a]}]
{5A==H;8B==H;9A==H;%
{13}B==CH$_{3}$;{14}A==H;{11}A==H}
```

The descriptor "11β,19" means that the configuration of C-19 (the methyl substituent at C-10) is specified implicitly by the parent name, 5α-androstane.

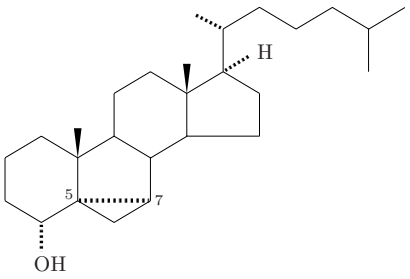
The linkage between the C-3 and the C-5 results in the formation of a cyclopropane ring as well as a cyclopentane ring. The linking bond is drawn by using `¥psline`, as shown in the following example.



3α,5-cyclo-5α-cholestan-6β-ol

```
¥steroidChain[{b¥null}%dummy
{b{¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1.5pt]%
(6,0)(336,0)}}]
{6B==OH;{10}B==¥null;{13}B==¥null;%
{17}GA==H;{20}A==¥null}
```

The linkage between the C-5 and the C-7 results in the formation of a cyclopropane ring as well as a cyclopentane ring. The linking bond is also drawn by using `¥psline`, as shown in the following example.

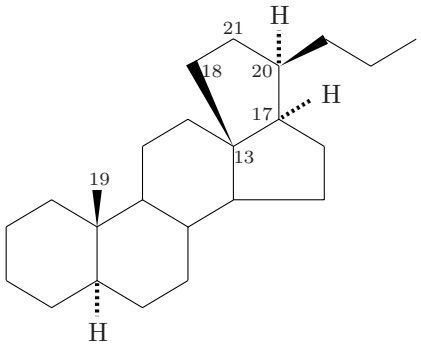


5,7α-cyclo-5α-cholestan-4α-ol

```
¥steroidChain[{b¥null}%dummy
{d{¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1.5pt]%
(6,0)(336,0)}}]
{4A==OH;{10}B==¥null;{13}B==¥null;%
{17}GA==H;{20}A==¥null}
```

The descriptor "3α,5" or "5,7α" means that the configuration at the C-5 is specified implicitly by the steroid name, so that the locant 5 needs not be attached by α or β. On the other hand, the basic name 5α-cholestan-4α-ol requires 5α.

The following structure is formed by means of a direct link between two carbon atoms of the steroid skeleton (C-18) and the attached side chain (C-21), as found in the descriptor "18,21-cyclo" of the IUPAC name. The bond between the C-13 and the C-18 is drawn by means of the `¥WedgeAsSubst` command, which is defined in Chapter 3 in the on-line manual of XyMTEX versions 4.02 and 4.03 (xymtx402403.pdf).



(20R)-18,21-cyclo-5α-cholane

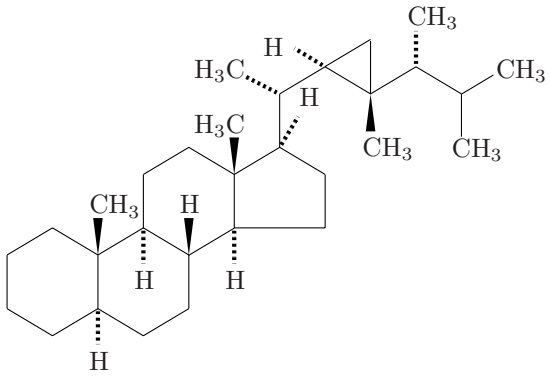
```
¥steroid[{T{¥sixfusev
{4s==¥WedgeAsSubst(0,0)(-1,2){158};
2s==¥WedgeAsSubst(0,0)(5,3){171};
2s==¥rput(171,103){%
¥trimethylenei{}{1==(yl)}}%
}{2FA==H}{c}[de]}}]
{5A==H;{10}B==¥null;{17}GA==H}
```

2.4.3 Additional Rings Formed within Side Chains

The formula of gorgostane is drawn by a rather dirty technique, which is based on nested ring fusions by `¥sixfusev` and `¥threefusehi`. Because the straight-forward function of ring fusion on a 17-side chain is not supported in XyMTEX, the side chain and the fused cyclopropane ring between C-22 and C-23 are drawn by using `¥sixfusev` which is combined with `¥threefusehi`. The construction of the side chain is represented by the nested scheme 6 ($\leftarrow$ 3) $\leftarrow$ 6. After the following definition of the command `¥gorgostane`,

```
¥def¥gorgostane{%
¥begin{XyMcompd}(1950,1350)(260,140){}{}
¥steroid[{s{¥sixfusev[%
{a{¥threefusehi{}{1Sd==H;2Su==CH$_{3}$}{a}}}%
{b{¥sixfusev{3==CH$_{3}$}{1A==CH$_{3}$;2==CH$_{3}$}{E}[cd]}}%
]{}{6A==H$_{3}$C}{D}[bc]}}]{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;{13}B==¥lmoiety{H$_{3}$C};%
{14}A==H;{17}SA==~H}
¥end{XyMcompd}}
```

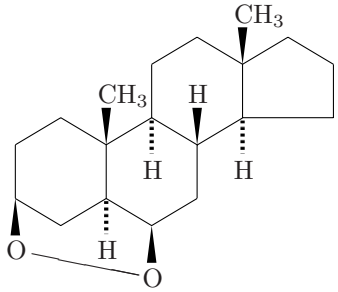
we use `¥gorgostane` so that the following formula is obtained:



2.4.4 Bridged Steroids

A peroxide bridge between non-adjacent positions of a steroid skeleton cannot be drawn by standard techniques supported by the XyMTEX system. But raw commands of the LaTeX 2_ε picture environment can be used in the arguments of XyMTEX commands. The following program involves the command `¥put(20,20){¥line(5,-1){403}}`, which draws a straight line between two oxygen atoms. For the nomenclature, see IUPAC-IUB (1989) 3S-10.1 [11].

LaTeX 2_ε compatible mode:

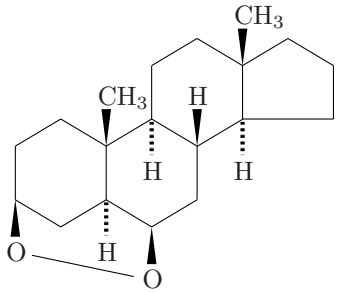


3β,6β-epidioxy-5α-androstane

```
¥steroid{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3FB==O¥put(20,20){¥line(5,-1){403}};6B==O}
```

Such a peroxide bridge can be also drawn by means of `¥psline` supported by the PSTricks system, which is automatically by calling the PostScript-compatible mode of the XyMTEX system. The optional arguments `unit=0.1pt` and `linewidth=0.4pt` of the `¥psline` command specifies the width of a line.

PostScript compatible mode:



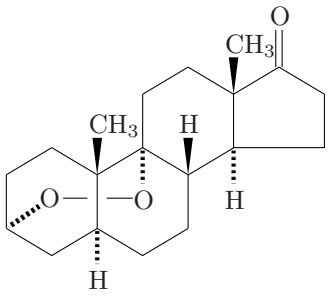
3β,6β-epidioxy-5α-androstane

```
¥steroid{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3FB==O¥rput(0,0){%
¥psline[unit=0.1pt,linewidth=0.4pt]%
(20,20)(403,-60)};6B==O}
```

Drawing a peroxide bridge between the C-3 and the C-9 requires a more complicated set of PSTricks commands. The optional arguments `linestyle=dashed` and `dash=1pt 1pt` of the `¥psline` command specify the properties of a dashed line for linking between the C-3 and the oxygen atom. Although the

¥psline is used in the argument of ¥rput in the following program, the ¥rput can be omitted after appropriate adjustment of output positions.

PostScript compatible mode:



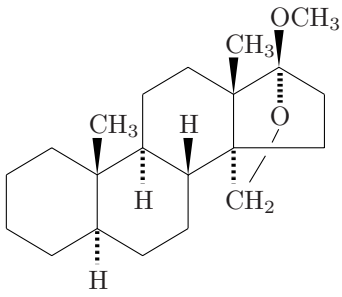
3α,9-epidioxy-5α-androstan-17-one

```
¥steroid{5A==H;{10}B==CH$_{3}$;8B==H;%
{13}B==CH$_{3}$;{14}A==H;{17}D==O;%
9A==O¥rput(0,0){%
¥psline[unit=0.1pt,linewidth=0.4pt]%
(-80,40)(-178,40)}%
¥rput(-171,0){%
¥psline[unit=0.1pt,linewidth=0.4pt]%
(-80,40)(-171,40)}%
¥rput(-392,40){¥makebox(0,0){O}}%
¥rput(-392,40){%
¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1pt]%
(-40,-30)(-155,-108)}}
```

As for the name of this derivative, the configuration at C-9 is implicitly determined to be 9α in terms of the name of 5α-androstane. As a result, the locant number 9 without α is contained in the above name.

A epoxymethano (O–CH_2) bridge linking C-17 and C-14 is recognized to form a tetrahydrofuran ring. The bridge is also drawn by the ¥psline command. For example, because the control position after the output of {14}A==CH$_{2}$ is the end of the CH_2 group, the position (-100,100) of the subsequent ¥psline is located at the upper right position of the C of the CH_2 group, from which the straight line due to the ¥psline starts, aiming at the (-40,200) position.

PostScript compatible mode:



17β-methoxy-17α,14-(epoxymethano)-5α-androstane

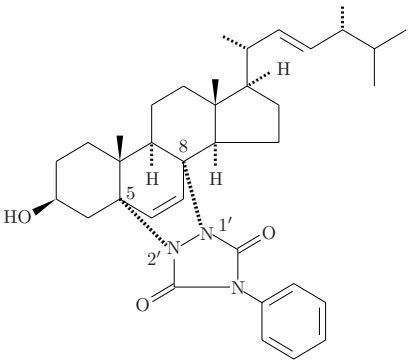
```
¥steroid{5A==H;{10}B==CH$_{3}$;8B==H;
9A==H;{13}B==CH$_{3}$;%
{14}A==CH$_{2}$%
¥psline[unit=0.1pt,linewidth=0.4pt]%
(-100,100)(-40,200)%
¥psline[unit=0.1pt,linewidth=0.4pt]%
(-15,250)(10,300)%
¥rput(15,350){¥makebox(0,0){O}}%
¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1pt]%
(15,400)(15,520);%
{17}B==OCH$_{3}$}
```

The configuration at C-14 is implicitly determined to be 14α in terms of the name of 5α-androstane so that the resulting name contains the locant number 14 without α.

The following structure shows a Diels-Alder adduct, which can be derived by a cycloaddition between an N=N double bond (at the N-1 and N-2 of 4-phenyl-[1,2,4]triazoline-3,5-dione) and the 5,7-diene moiety (at the C-5 and C-8 terminals of the diene moiety of ergosterol). The descriptor "5,8-[1,2]" indicates the location of the Diels-Alder addition. To specify substitution positions in the Diels-Alder adduct, the locants of the steroid skeleton is denoted by an integer without a prime, while those of the triazolinedione is denoted by an integer with a prime.

PostScript compatible mode:

(22E)-3β-hydroxy-4$'$-phenyl-5,8-[1,2]epi[1,2,4]triazolo-5α,8α-ergosta-6,22-diene-3$'$,5$'$-dione



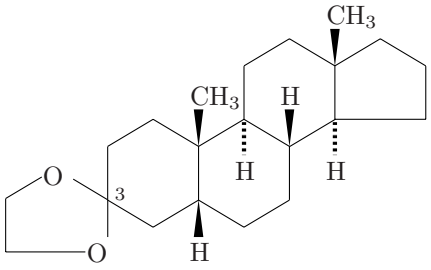

```
¥begin{XyMcompd}(2100,1900)(0,-500){}{}
¥steroidChain[f{Zc}%
{d{%
¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1pt]%
(0,0)(250,-250)%
¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1pt]%
(435,-140)(342,200)%
¥rput(250,-250){¥fiveheterovi{1==N;3==N;5==N}%
{5==(yl);2D==O;4D==O;3==¥bzdrv{6==(yl)}}}}}]%
{3B==HO;9A==H;%
{10}B==¥null;{13}B==¥null;{14}A==H;%
{17}GA==H;%
{20}A==¥null;{24}A==¥null}
¥end{XyMcompd}
```

The "5,8-[1,2]" moiety of the structure is drawn by using `¥psline` and `¥rput`, where the inner original point `(0,0)` is located at the C-5 (i.e., the terminal carbon of the double bond denoted by `d`). The dashed lines between 5 and 2$'$ and between 8 and 1$'$ are specified by the optional arguments `linestyle=dashed` and `dash=1pt 1pt` of the `¥psline` command.

2.4.5 Steroids with Spiro Rings

The macros for drawing steroids in the present status do not support the atomlist functions so that spiro rings attached on the steroid skeleton cannot be directly drawn by using such atomlists. There are three alternative (non-standard) methods for drawing steroid with spiro rings.

The first method is a rather forcible one, where a spiro unit (`¥fiveheterovi`) is described in the substlist (the main argument as a substituent list) as follows:

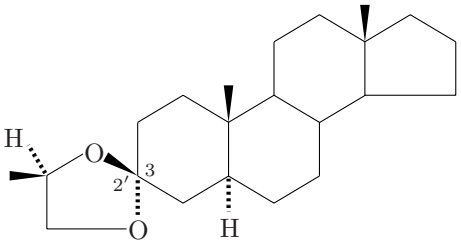


5β-androstane-3-one ethylene acetal

```
¥steroid{5B==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3F==¥raisebox{-80¥unitlength}{%
¥fiveheterovi{1==O;3==O}{3==(yl)}[ab]};%
3G==}
```

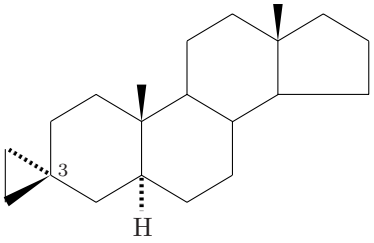
According to the traditional nomenclature, the above compound is named as an acetal (ketal) of 5β-androstane-3-one, which may be reacted with ethylene glycol so as to produce the ethylene acetal.

The second method for drawing spiro-steroids is a more plausible one, which uses the optional argument for treating unsaturation. For example, the descriptor `b` (or `B`) for designating a double bond between the C-2 and C-3 utilizes the x, y-coordinates of the C-3 (or C-2) during the process of setting the double bond. Hence, we can put a spiro ring (due to the `fiveheterovi` command or `threeheterovi`) on the C-3 atom by virtue of the descriptor `b`, as exemplified by the following two structures.



(4′*R*)-4′-methyl-(3*S*)-spiro[5α-androstane-3,2′-[1,3]dioxolane]

```
¥steroid[%
{b{¥fiveheterovi({bA}){1==O;3==O}%
{2==(yl);5Su==¥null;5Sd==H}[a]}}%
{b{¥WedgeAsSubst(0,0)(-5,3){120}}}]
{5A==H;{10}B==¥null;{13}B==¥null}
```

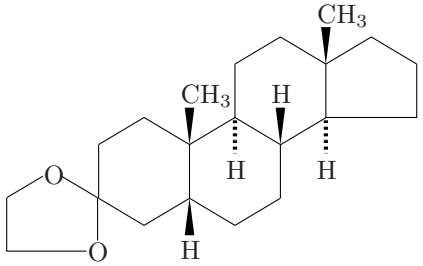


spiro[5α-androstane-3,1′-cyclopropane]
also 3,3-ethylene-5α-androstane

```
¥steroid[%
{b{¥threeheteroh({cA}){}{1==(yl)}[a]}}%
{b{¥WedgeAsSubst(0,0)(-5,-3){168}}}]
{5A==H;{10}B==¥null;{13}B==¥null}
```

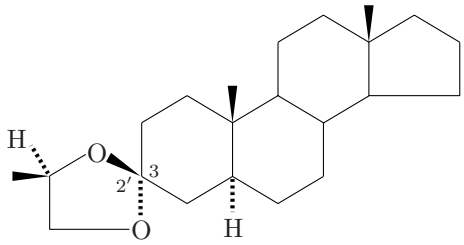
The names of the two compounds shown above are based on the nomenclature for spiro union. For example, the name "spiro[···-3,2′-···]" means that the position 3 of the first unit (5α-androstane for ···) is linked the the position 2′ of the second unit ([1,3]dioxolane for ···).

The third method for drawing spiro-steroids is a more systematic one, where the atomlist of a spiro ring (e.g., `¥fiveheterovi`) is used to put a steroid moiety as substituent. The code `2s==¥steroid{3==(yl);` in the steroid moiety specifies the joint position of the spiro union, which is represented by "spiro[···-3,2′-···]" in the IUPAC name.



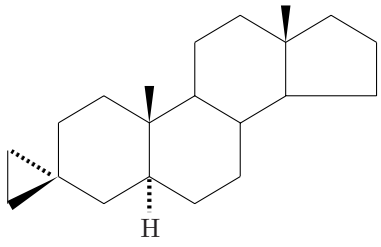
5β-androstane-3-one ethylene acetal

```
¥begin{XyMcompd}(1450,1000)(250,300){}{}
¥fiveheterovi{1==O;3==O;2s==¥steroid%
{3==(yl);5B==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H}}{}
¥end{XyMcompd}
```



(4′*R*)-4′-methyl-(3*S*)-spiro[5α-androstane-3,2′-[1,3]dioxolane]

```
¥begin{XyMcompd}(1500,900)(-400,-200){}{}
¥fiveheterovi({bA})
[{b{¥WedgeAsSubst(0,0)(-5,3){120}}}]
{1==O;3==O;%
2s==¥steroid{3==(yl);5A==H;%
{10}B==¥null;{13}B==¥null}}%
{2==(yl);5Su==¥null;5Sd==H}[a]%
¥end{XyMcompd}
```



spiro[5α-androstane-3,1′-cyclopropane]
also 3,3-ethylene-5α-androstane

```
¥begin{XyMcompd}(1250,800)(300,150){}{}
¥threeheteroh({cA})%
{1s==¥steroid{3==(yl);5A==H;%
{10}B==¥null;{13}B==¥null};
1s==¥WedgeAsSubst(0,0)(-5,-3){183}}{}[a]%
¥end{XyMcompd}
```

2.5 Vitamin D_2

Irradiation of ergosterol (and lumisterol) described in Subsection 2.3.2 causes the opening of the B ring to produce previtamin D_2 having a conjugated triene, which is a precursor of vitamin D_2 (ergocalciferol), as shown in Fig. 2.1.

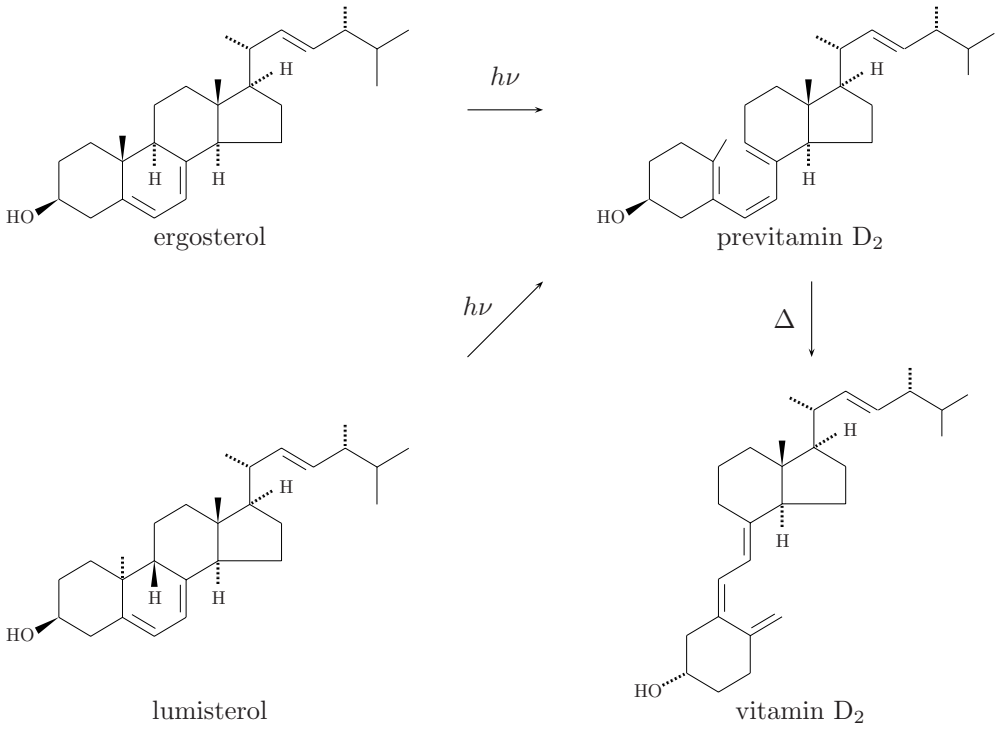


Figure 2.1: Photochemistry of ergosterol and lumisterol

These two photochemical conversions are conrotatory pericyclic processes, which are symmetry-allowed [12, Section 5.1] and proceed smoothly because of no steric hindrance between the 10β methyl and the 9α hydrogen in ergosterol and between the 10α methyl and the 9β hydrogen in lumisterol. On the other hand, the 9β,10β-isomer ((22E)-9β,10β-ergosta-5,7,22-trien-3β-ol) and the 9α,10α-isomer ((22E)-9α,10α-ergosta-5,7,22-trien-3β-ol) do not undergo such ring openings because of steric hindrance, although these conrotatory pericyclic processes are symmetry-allowed. Instead, the 9β,10β-isomer and the 9α,10α-isomer undergo other symmetry-allowed photochemical processes so as to give cyclobutene rings.

To draw the scheme shown in Fig. 2.1, the programs for drawing lumisterol and ergosterol shown in Subsection 2.3.2 are used to define `¥lumisterol` and `¥ergosterol` as follows:

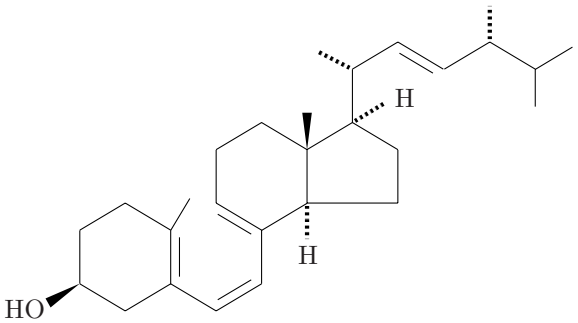
```
¥def¥lumisterol{%
¥begin{XyMcompd}(2050,1150)(0,250){}{}
¥steroidChain[eg{Zc}]%
{3B==HO;9B==H;{10}A==¥null;%
{13}B==¥null;{14}A==H;{17}GA==H;%
{20}A==¥null;{24}A==¥null}
¥end{XyMcompd}
}

¥def¥ergosterol{%
```

```
¥begin{XyMcompd}(2050,1150)(0,250){}{}
¥steroidChain[eg{Zc}]%
{3B==HO;9A==H;{10}B==¥null;%
{13}B==¥null;{14}A==H;{17}GA==H;%
{20}A==¥null;{24}A==¥null}
¥end{XyMcompd}
}
```

The command ¥previtaminD is defined to draw the intermediate, previtamin D_2. The command consists of a multiple nested fusion, which is schematically represented by $6 \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6 \leftarrow 3$. The last step ($\leftarrow 3$) is an application of the technique for drawing a spiro compound.

```
¥def¥previtaminD{%
¥begin{XyMcompd}(2050,1150)(0,250){}{}
¥sixheterov[{b{¥sixfusev[ace%
{a{¥sixfusev[{b{¥fivefusevi[{a{¥sixfusev[a]{%
2s==¥trimethylene{}{1==(yl);2A==¥null;3==¥null;3W==¥null}
}{6A==¥null}{D}[bc]}}]{}{1GA==H}{D}}}%
]{}{2FB==¥null;3GA==H}{D}}}]{}{}{E}[f]}}]%
{}{2Sb==¥null;5B==HO}
¥end{XyMcompd}
}
```

Output of ¥previtaminD without size reduction:

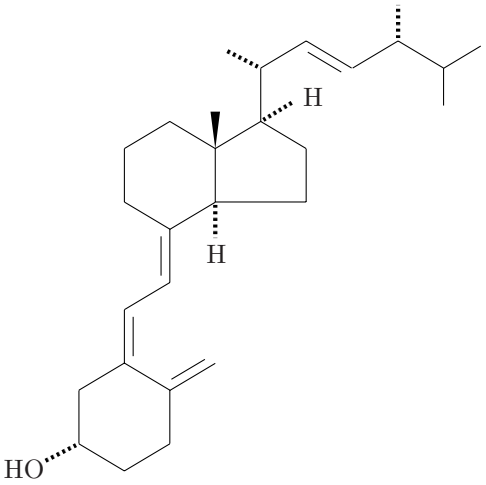


(6*Z*, 22*E*)-(3*S*)-9,10-secoergosta-5(10),6,8,22-tetraen-3-ol
(previtamin D_2)

To draw vitamin D_2 (ergocalciferol), the command ¥vitaminDii is defined as follows. The command consists of a multiple nested fusion, which is schematically represented by $6 \leftarrow 6 \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6 \leftarrow 3$. The last three steps ($6 \leftarrow 5 \leftarrow 6 \leftarrow 3$) are common to the command ¥previtaminD.

```
¥def¥vitaminDii{%
¥begin{XyMcompd}(1650,1750)(0,250){}{}
¥sixheterov[{a{¥sixfusev[ce%
{f{¥sixfusev[b%
{a{¥sixfusev[
{b{¥fivefusevi[
{a{¥sixfusev[a]{%
2s==¥trimethylene{}{1==(yl);2A==¥null;3==¥null;3W==¥null}
}{6A==¥null}{D}[bc]}}
]{}{1GA==H}{D}}}
]{}{2FB==¥null;3GA==H}{D}
}}
]{}{}{C}[def]}}]{}{}{D}[ab]}}]{}{5A==HO}
¥end{XyMcompd}
}
```

Output of ¥vitaminDii without size reduction:



$(5Z, 7E, 22E)$-(3S)-9,10-secoergosta-5,7,10(19),22-tetraen-3-ol
(vitamin D_2 or ergocalciferol)

Finally, the newly-defined commands are arranged by using the LaTeX 2_ε `tabular` environment, where the size of each formula is reduced by means of ¥scalebox supported by the graphicx package. The commands ¥reactrarrow, ¥reactnearrow, and ¥reactdarrow, which are defined in the chemist package, are used to draw arrows representing chemical reactions.

```
¥begin{tabular}{ccc}
¥scalebox{0.7}{¥ergosterol} &
¥reactrarrow{0pt}{1cm}{$h¥nu$}{¥strut} & ¥scalebox{0.7}{¥previtaminD} ¥¥
ergosterol & & previtamin D$_{2}$ ¥¥[10pt]
& ¥reactnearrow{0pt}{1cm}{¥raisebox{10pt}{¥rlap{$h¥nu$}}}{¥strut} &
¥reactdarrow{0pt}{1cm}{$¥Delta$}{¥strut}  ¥¥
¥scalebox{0.7}{¥lumisterol} && ¥scalebox{0.7}{¥vitaminDii} ¥¥
lumisterol & & vitamin D$_{2}$
¥end{tabular}
```

The output of this tabulated scheme is shown in Fig. 2.1.

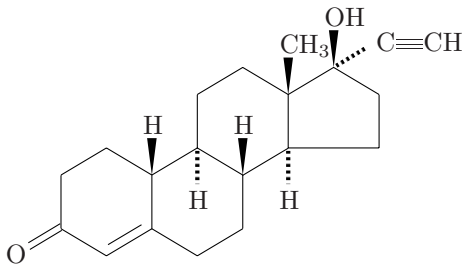
Chapter 3

Parent Structures for Steroids

3.1 Fundamental Parent Structures without a 17-Side Chain

A fundamental parent structure for a series of steroids is selected to be nearly full saturated and to contain acyclic hydrocarbon groups that occur in most of the series. Table 3.1 lists the commands for drawing gonanes and estranes, which are most fundamental parent structures without a 17-side chain. They are differentiated according to the presence or absence of methyl groups at C-10 and C-13.

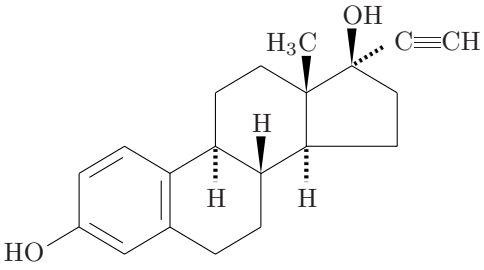
The formula of norethindrone (or norethinsterone), which is used as a component of some combined oral contraceptive pills, is drawn by means of the command `¥estrane`.



17α-ethynyl-17β-hydroxyestr-4-en-3-one
norethindrone (or norethinsterone)

```
¥begin{XyMcompd}(1700,1100)(0,150){}{}
¥estrane[d]{3D==O;{17}B==OH;%
{17}GA=={C¥triplebond CH}}
¥end{XyMcompd}
```

The formula of ethynylestradiol, which is also used as a component of some combined oral contraceptive pills, is drawn by means of the command `¥steroid` in place of the command `¥estrane`, because the latter command draws the 10β-hydrogen automatically.

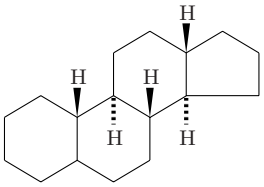
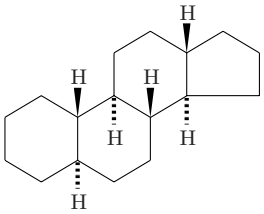
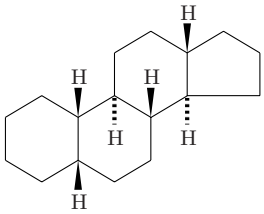
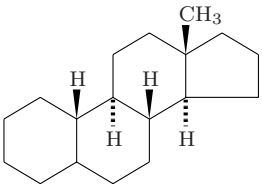
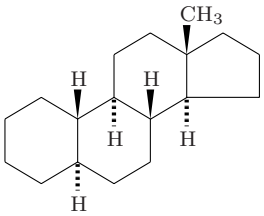
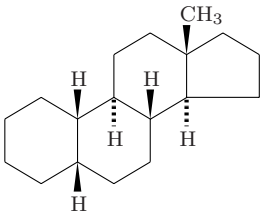
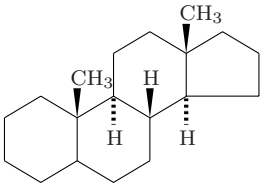
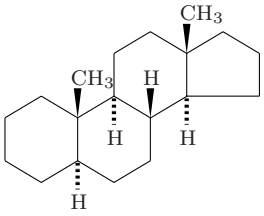
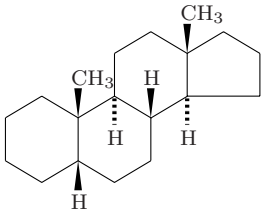


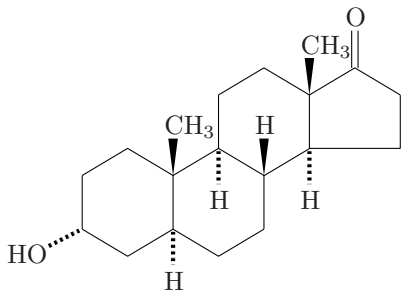
17α-ethynylestra-1,3,5(10)-triene-3,17β-diol
ethynylestradiol

```
¥begin{XyMcompd}(1700,1100)(0,150){}{}
¥steroid[ack]{3==HO;8B==H;9A==H;%
{13}B==¥lmoiety{H$_{3}$C};{17}B==OH;%
{14}A==H;{17}GA=={C¥triplebond CH}}
¥end{XyMcompd}
```

Androsterone is the first isolated androgen (male sex hormone). The structural formula is drawn by the command `¥androstanealpha`.

Table 3.1: Gonanes, Estranes and Androstanes

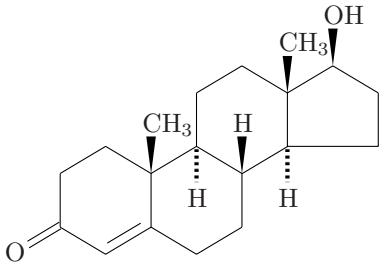
5-unspecified	5α series	5β series
		
`¥gonane{}`	`¥gonanealpha{}` 5α-gonane	`¥gonanebeta{}` 5β-gonane
		
`¥estrane{}`	`¥estranealpha{}` 5α-estrane	`¥estranebeta{}` 5β-estrane
		
`¥androstane{}`	`¥androstanealpha{}` 5α-androstane	`¥androstanebeta{}` 5β-androstane



3α-hydroxy-5α-androstan-17-one
androsterone

```
¥androstanealpha{3A==HO;{17}D==O}
```

However, testosterone isolated later was found to be a true male sex hormone (androgen), which promotes the development of secondary male characteristics such as the growth of facial and body hair and muscular development. Androsterone is a metabolized form of testosterone so as to be excreted in the urine. The structural formula of testosterone is drawn by using the `¥androstane` command as follows:

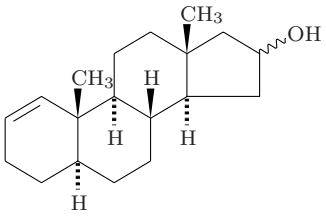


17β-hydroxyandrost-4-en-3-one
testosterone

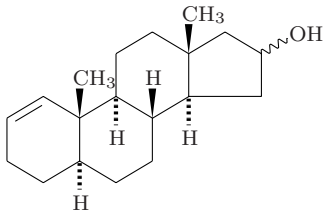
```
¥androstane[d]{3D==O;{17}B==OH}
```

An alternative program for drawing testosterone has been described in the preceding chapter (Use of the prefix *ent-*).

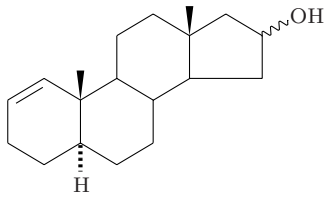
The formula of 5α-androst-1-en-16ξ-ol is drawn in two ways by using `¥androstane` (for an unspecified 5-configuration) and `¥androstanealpha` (for a 5α-configuration):




```
¥androstane[a]{5A==H;
{16}U==OH}
```




```
¥androstanealpha[a]
{{16}U==OH}
```

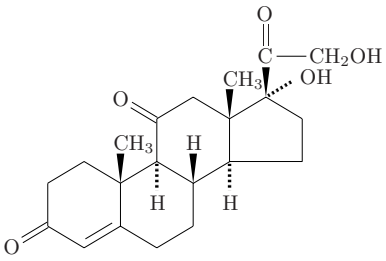



```
¥steroid[a]{5A==H;
{10}B==¥null;
{13}B==¥null;{16}U==OH}
```

5α-androst-1-en-16ξ-ol

The implicit configurations of hydrogens at C-8, C-9, and C-14 are permitted to be omitted. To draw such a simplified formula, we start from the basic command `¥steroid` without no modifiers, as exemplified in the last structure.

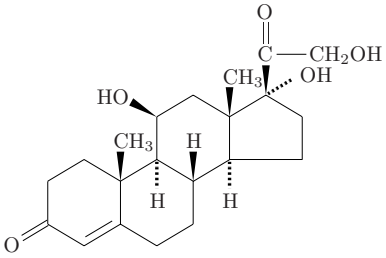
Adrenocortical hormones secreted from the adrenal cortex include steroid derivatives. The adrenocortical steroids are involved in the regulation of biological activities such as the metabolism of carbohydrate, protein, and lipid. The formula of cortisone, which is an adrenocortical hormone, is drawn by using the command `¥androstane`.



17α,21-dihydroxypregn-4-ene-3,11,20-trione
cortisone

```
¥begin{XyMcompd}(1700,1300)(0,150){}{}
¥androstane[d]{3D==O;{11}D==O;%
{17}GA==OH;%
{17}B==¥tetrahedral{3==(yl);%
O==C;1D==O;4==CH$_{2}$OH}}
¥end{XyMcompd}
```

The formula of cortisol (hydrocortisone), which is an active form of cortisone, is drawn also by using the command `¥androstane`.



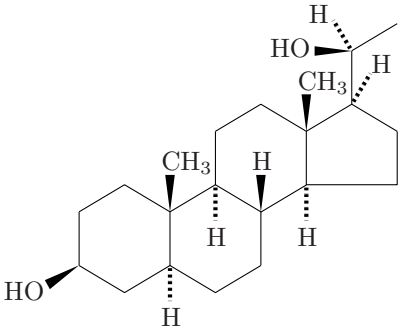
11β,17α,21-trihydroxypregn-4-ene-3,20-dione
cortisol (hydrocortisone)

```
¥begin{XyMcompd}(1700,1300)(0,150){}{}
¥androstane[d]{3D==O;{11}B==HO;%
{17}GA==OH;%
{17}B==¥tetrahedral{3==(yl);%
O==C;1D==O;4==CH$_{2}$OH}}
¥end{XyMcompd}
```

3.2 Fundamental Parent Structures with a Short 17-Side Chain

Table 3.2 lists the commands for drawing pregnanes and cholanes, which are fundamental parent structures having a short side chain at the C-17 of the steroid skeleton.

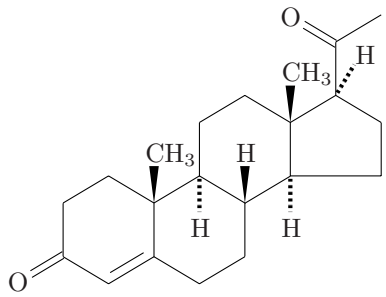
The following structure can be drawn by using the command `¥pregnanealpha` with a filled substlist, where the implicit substituents at 10β, 13β, etc. are printed automatically even if unspecified.



(20*S*)-5α-pregnan-3β,20-diol

```
¥begin{XyMcompd}(1400,1200)(0,150){}{}
¥pregnanealpha{3B==HO;{20}Su==HO;{20}Sd==H}
¥end{XyMcompd}
```

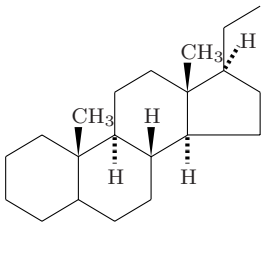
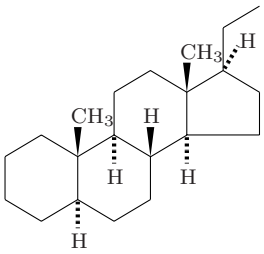
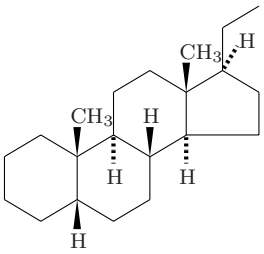
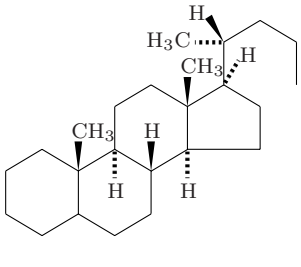
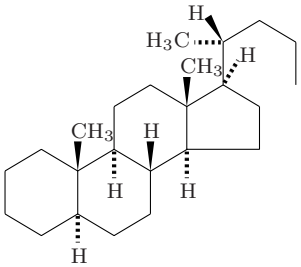
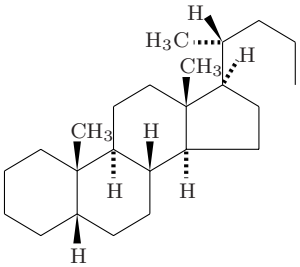
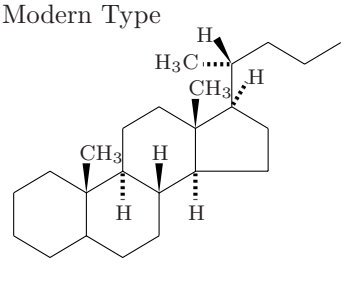
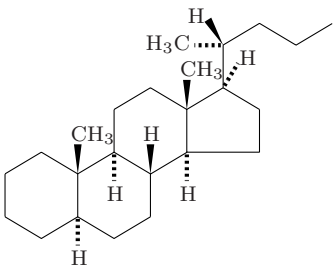
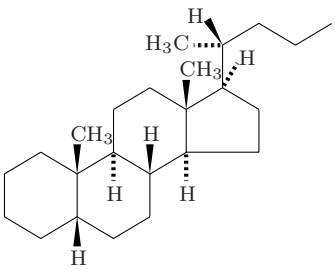
Progesterone, which is an important progestin (pregnancy hormone), is secreted after ovulation occurs to prepare the lining of the uterus for implantation of the fertilized ovum and to complete pregnancy. The formula of progesterone is drawn by using the command `¥pregnane`.



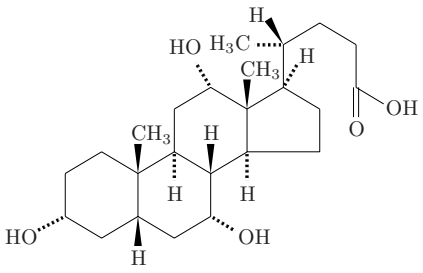
pregn-4-ene-3,20-dione
progesterone

```
¥pregnane[d]{3D==O;{20}D==O}
```

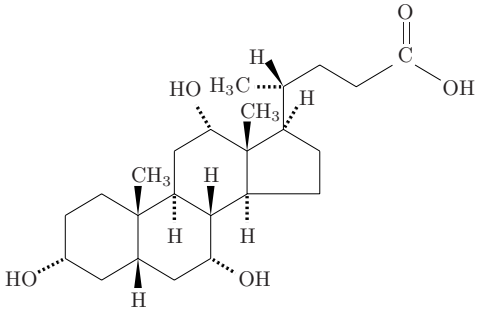
Table 3.2: Pregnanes and Cholanes

5-unspecified	5α series	5β series
		
`¥pregnane{}`	`¥pregnanealpha{}` 5α-pregnane	`¥pregnanebeta{}` 5β-pregnane
		
`¥cholanE{}`	`¥cholanealpha{}` 5α-cholane	`¥cholanebeta{}` 5β-cholane
Modern Type		
		
`¥cholane{}`	`¥cholaneAlpha{}` 5α-cholane	`¥cholaneBeta{}` 5β-cholane

The formula of cholic acid, which is a bile acid, is drawn by using the command ¥pregnanealpha or ¥pregnaneAlpha. The latter command should be combined with a dirty technique during placing a COOH group at the terminal position of the side chain.



```
¥cholanebeta
{3A==HO;7A==OH;{12}Sd==¥lmoiety{HO};%
{24}D==O;{24}F==OH}
```



```
¥cholaneBeta[{s¥null}%
{s{¥rput(513,303){%
¥Dtrigonal{3==(yl);O==C;1D==O;2==OH}}}}]
{3A==HO;7A==OH;{12}Sd==¥lmoiety{HO}}
```

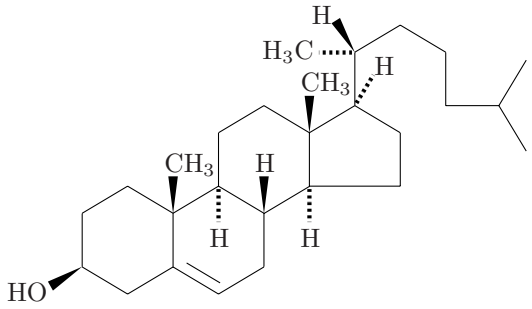
3α,7α,12α-trihydroxy-5β-cholan-24-oic acid
cholic acid

3.3 Fundamental Parent Structures with a 17-Side Chain

3.3.1 Chain Folding of Classical Type

Table 3.3 lists the commands for drawing cholestanes, ergostanes, and campestanes, which are fundamental parent structures having a side chain of classical-type folding at the C-17 of the steroid skeleton. The bond between C-22 and C-23 is suitable for drawing a cisoid double bond.

Although cholesterol occurs widely in the body, the full information on its biological functions is not yet obtained. The formula of cholesterol is drawn by using the command ¥cholestanE, which gives a 17-side chain of classical-type folding.

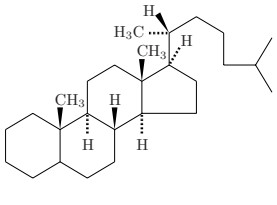
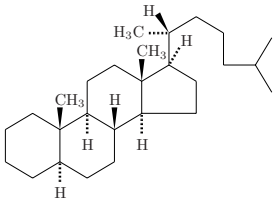
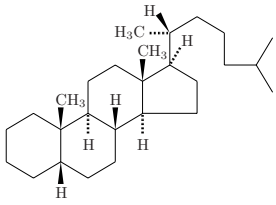
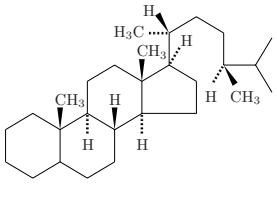
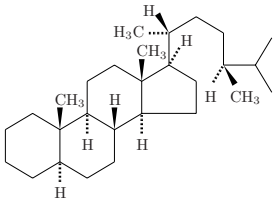
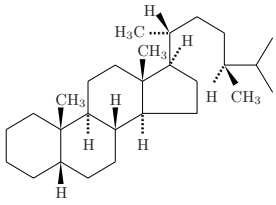
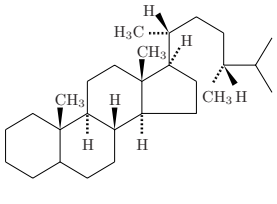
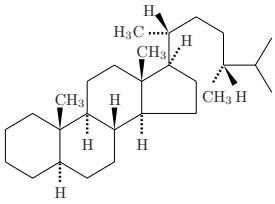
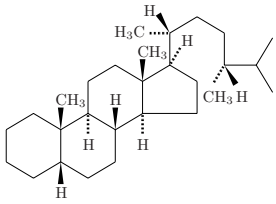
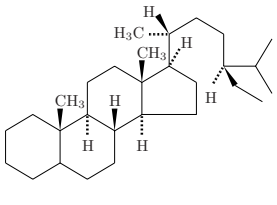
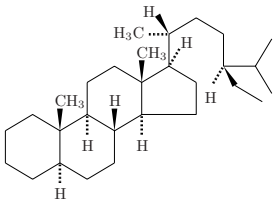
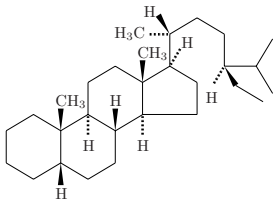
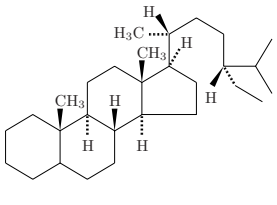
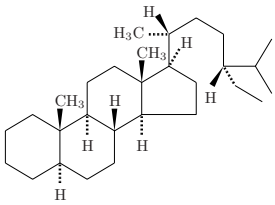
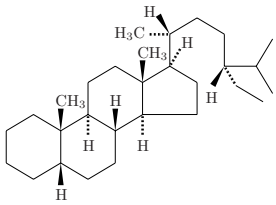


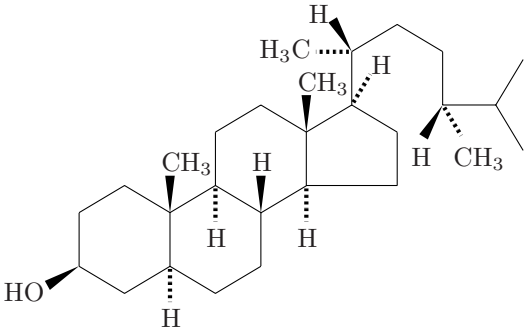
cholest-5-en-3β-ol
(cholesterol)

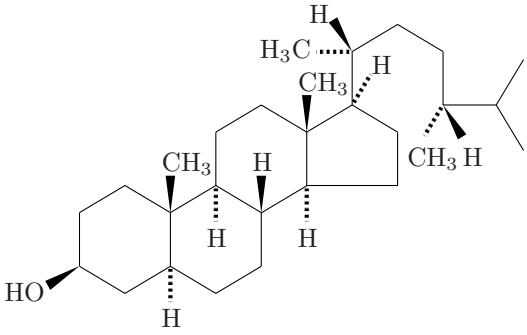
```
¥cholestanE[e]{3B==HO}
```

The formula of campestanol is drawn by ¥cholestanealpha or ¥campestanealpha.

Table 3.3: Cholestanes, Ergostanes, Campestanes, etc. with Chain Folding of Classical Type

5 unspecified	5α series	5β series
		
`¥cholestanE{}`	`¥cholestanealpha{}` 5α-cholestane	`¥cholestanebeta{}` 5β-cholestane
		
`¥ergostanE{}`	`¥ergostanealpha{}` 5α-ergostane	`¥ergostanebeta{}` 5β-ergostane
		
`¥campestanE{}`	`¥campestanealpha{}` 5α-campestane	`¥campestanebeta{}` 5β-campestane
		
`¥poriferastanE{}`	`¥poriferastanealpha{}` 5α-poriferastane	`¥poriferastanebeta{}` 5β-poriferastane
		
`¥stigmastanE{}`	`¥stigmastanealpha{}` 5α-stigmastane	`¥stigmastanebeta{}` 5β-stigmastane



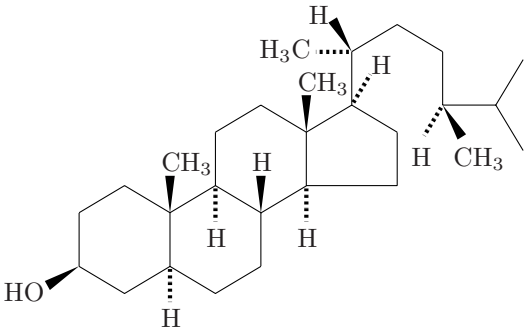


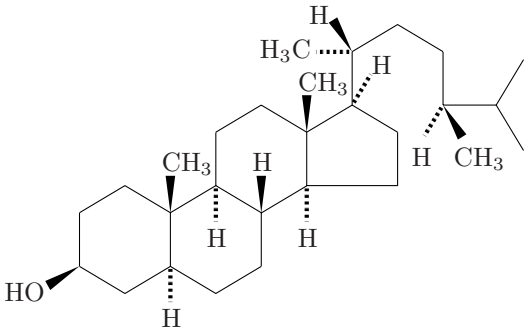
```
¥cholestanealpha{3B==HO;%
{24}SA==CH$_{3}$;{24}SB==H}
```

```
¥campestanealpha{3B==HO}
```

(24*R*)-24-methyl-5α-cholestan-3β-ol (trivial name: campestanol)

Similarly, two ways for drawing ergostanol are shown as follows:



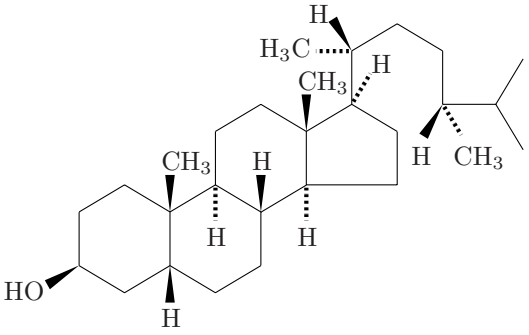


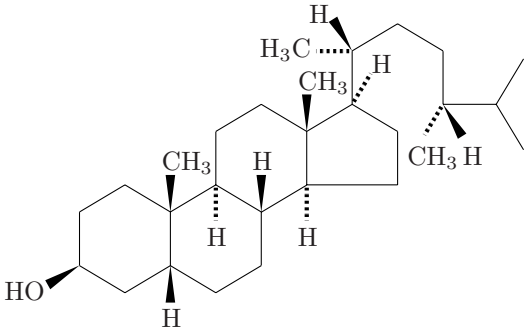
```
¥cholestanealpha{3B==HO;%
{24}Su==CH$_{3}$;{24}Sd==H}
```

```
¥ergostanealpha{3B==HO}
```

(24*S*)-24-methyl-5α-cholestan-3β-ol (trivial name: ergostanol)

The formula of a 5β isomer is drawn by `¥cholestanebeta` or `¥campestanebeta`.





```
¥cholestanebeta{3B==HO;%
{24}SA==CH$_{3}$;{24}SB==H}
```

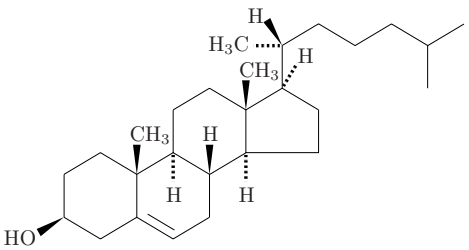
```
¥campestanebeta{3B==HO}
```

(24*R*)-24-methyl-5β-cholestan-3β-ol

3.3.2 Chain Folding of Modern Type

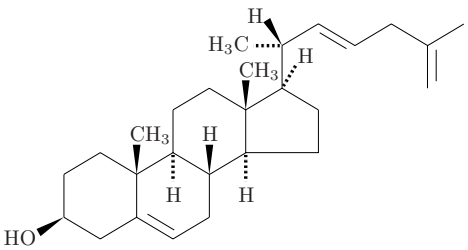
Table 3.4 lists the commands for drawing cholestanes, ergostanes, and campestanes, which are fundamental parent structures having a side chain of modern-type folding at the C-17 of the steroid skeleton.

The bond between C-22 and C-23 is suitable for drawing a transoid (22*E*) double bond, as found in the second formula below.



```
¥cholestane[e]{3B==HO}
```

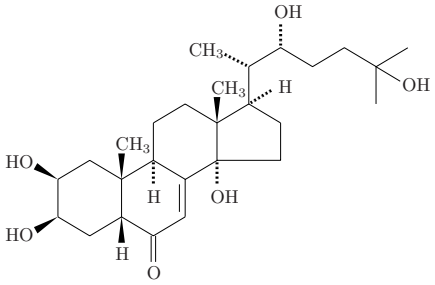
cholest-5-en-3β-ol
(cholesterol)



```
¥cholestane[e{Zc}{Zg}]{3B==HO}
```

(22*E*)-cholesta-5,22,25-trien-3β-ol

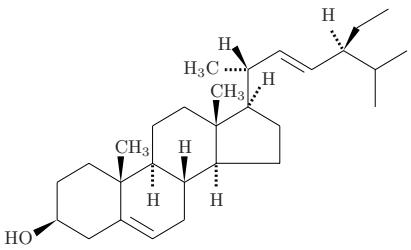
Even if a compound has a systematic name based on cholestane, the command `¥steroidChain` is sometimes necessary to complete a correct structure. For example, the following structure of ecdysone shows that the 7-ene is inconsistent with the 8β-hydrogen of the command `¥cholestane`, which hence cannot be used for this purpose.



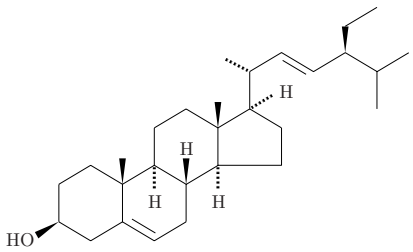
(22*R*)-2β,3β,14,22,25-pentahydroxy-5β-cholest-7-en-6-one
ecdysone

```
¥steroidChain[g]{%
2B==HO;3B==HO;5B==H;6D==O;
9A==H;{10}B==CH$_{3}$;
{13}B==CH$_{3}$;{14}A==OH;
{17}GA==H;{20}A==CH$_{3}$;
{22}A==OH;{{25}}==OH}
```

Stigmasterol is a plant steroid, which is obtained commercially from soybean oil. The 22*E*-olefinic function requires the command for drawing a 17-side chain of modern-type folding. Its formula is drawn by using the command `¥stigmastane` or `¥steroidChain`.



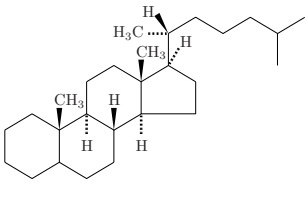
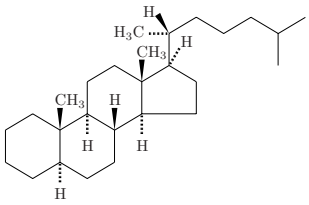
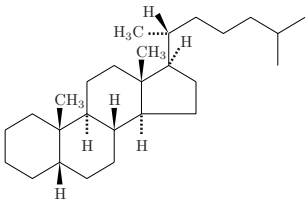
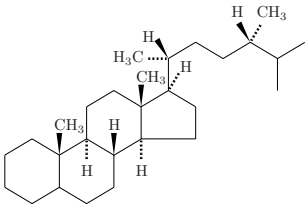
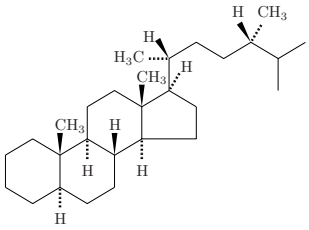
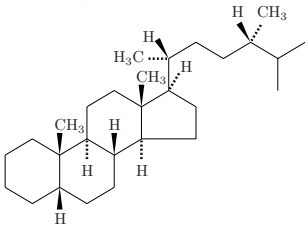
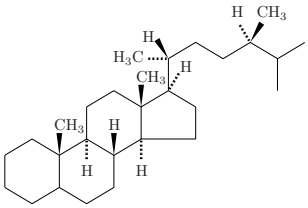
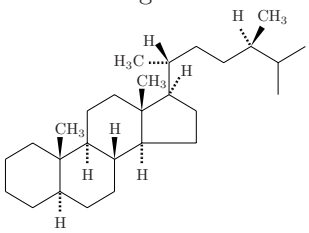
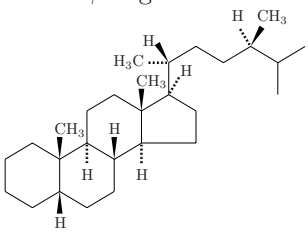
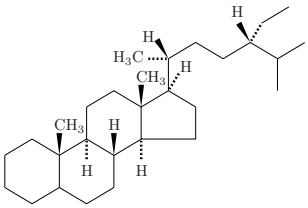
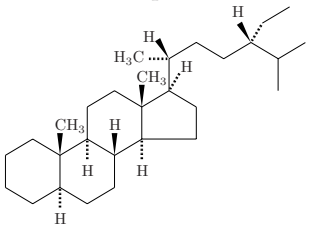
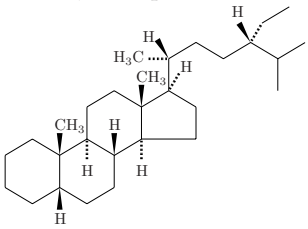
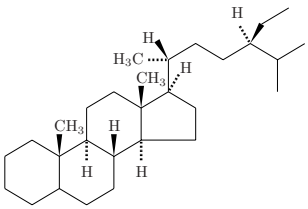
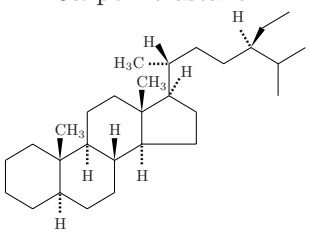
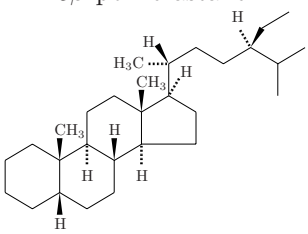
```
¥stigmastane[e{Zc}]{3B==HO}
```



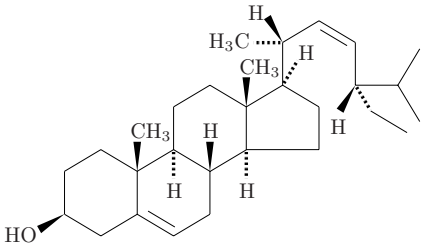
```
¥steroidChain[e{Zc}]{3B==HO;8B==H;%
9A==H;{10}B==¥null;{13}B==¥null;%
{14}A==H;{20}A==¥null;%
{17}GA==H;{24}B==%
¥dimethylene{}{1==(yl)}}} ¥¥
```

(22*E*)-stigmasta-5,22-dien-3β-ol (stigmasterol)

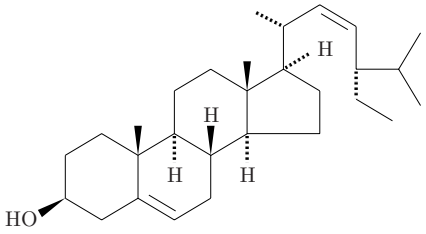
Table 3.4: Cholestanes, Ergostanes, Campestanes, etc. with Chain Folding of Modern Type

5 unspecified	5α series	5β series
		
`¥cholestane{}`	`¥cholestaneAlpha{}` 5α-cholestane	`¥cholestaneBeta{}` 5β-cholestane
		
`¥ergostane{}`	`¥ergostaneAlpha{}` 5α-ergostane	`¥ergostaneBeta{}` 5β-ergostane
		
`¥campestane{}`	`¥campestaneAlpha{}` 5α-campestane	`¥campestaneBeta{}` 5β-campestane
		
`¥poriferastane{}`	`¥poriferastaneAlpha{}` 5α-poriferastane	`¥poriferastaneBeta{}` 5β-poriferastane
		
`¥stigmastane{}`	`¥stigmastaneAlpha{}` 5α-stigmastane	`¥stigmastaneBeta{}` 5β-stigmastane

The 22Z-olefinic function requires the command for drawing a 17-side chain of classical-type folding. Two different expressions with and without designating methyl substituents explicitly are depicted as follows. Its formula is drawn by using the command ¥stigmastanE or ¥steroidchain.




```
¥stigmastanE[e{Zc}]{3B==HO}
```




```
¥steroidchain[e{Zc}]{3B==HO;%
8B==H;9A==H;%
{10}B==¥null;{13}B==¥null;%
{14}A==H;{20}A==¥null;%
{17}GA==H;{24}A==%
¥dimethylenei{}{1==(yl)}}
```

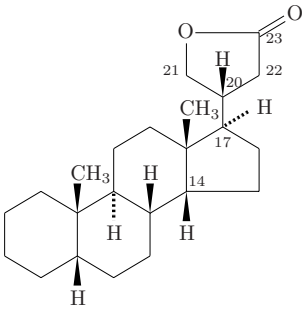
(22Z)-stigmasta-5,22-dien-3β-ol

Chapter 4

Steroids with Heterocyclic Substituents

4.1 Cardanolides

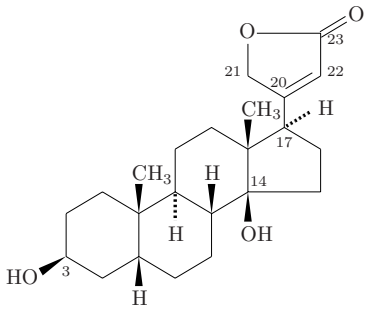
The formula of 5β-cardanolide is drawn by using `¥steroid`, where the 14β-configuration and the 20R-configuration are implicitly determined in the name. Note that the configuration of C-20 is the same as that of the C-20 of cholesterol, as the locants indicate. The formation of the lactone ring does not suffer the specification of RS-stereodescriptors at the C-20. The priority sequence 21(OHH) > 17(CCH) > 22 (CHH) > H for 5β-cardanolide provides an R-stereodescriptor just as the counterpart 17(CCH) > 22(CHH) > 21 (HHH) > H for cholesterol provides an R-stereodescriptor.



5β-cardanolide

```
¥begin{XyMcompd}(1300,1400)(250,150){}{}
¥steroid{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;%
{{17}}==¥fiveheterov{4==O;%
1s==¥WedgeAsSubst(0,0)(0,1){140};%
1s==¥rput(0,180){H}}{1==(yl);3D==O}}
¥end{XyMcompd}
```

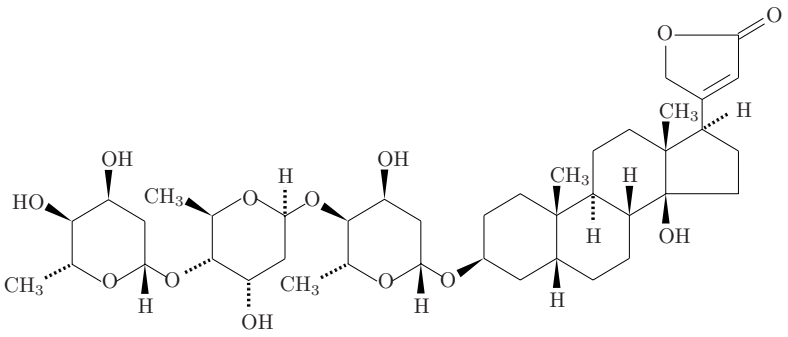
The formula of digitoxigenin, which is a cardiac aglycon isolated by hydrolysis of digitalis, is drawn by using `¥steroid`.



3β,14-dihydroxy-5β-card-20(22)-enolide
digitoxigenin

```
¥begin{XyMcompd}(1500,1400)(50,150){}{}
¥steroid{3B==HO;5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
¥end{XyMcompd}
```

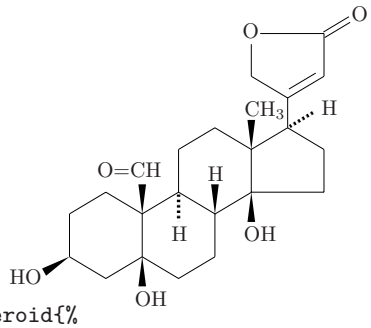
Digitalis contains digitoxigenin in the form of a cardiac glycoside, which is known as digitoxin. The sugar molecules joined in acetal linkages to the 3-OH of digitoxigenin can be drawn by using three nested `¥lyl` commands so as to complete the formula of digitoxin as follows:



digitoxin

```
¥begin{XyMcompd}(3600,1500)(-2000,50){}{}
¥steroid{%
3B==¥lyl(3==O){3==¥sixheterovi{1==O}{2==(yl);2GB==H;4B==OH;6A==CH$_{3}$;%
5B==¥lyl(5==O){5==¥sixheterov{1==O}{2==(yl);2FA==H;4A==OH;6B==CH$_{3}$;%
5A==¥lyl(3==O){3==¥sixheterovi{1==O}{2==(yl);2GB==H;4B==OH;6A==CH$_{3}$;5B==HO}}%
}}}};%
5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
¥end{XyMcompd}
```

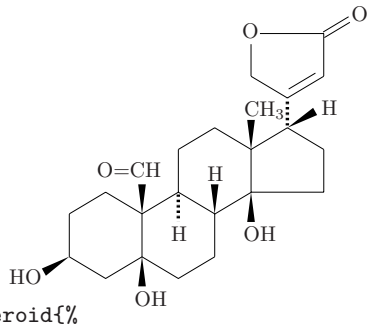
The structural formulas of strophanthidin and 17α-strophanthidin are drawn by using `steroid`, where `¥rput(-30,50){O=CH}` is used to adjust the position of the C-10 substituent.



```
¥steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==¥rput(-30,50){O=CH};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
```

strophanthidin

3β,5,14-trihydroxy-19-oxo-5β-card-20(22)-enolide



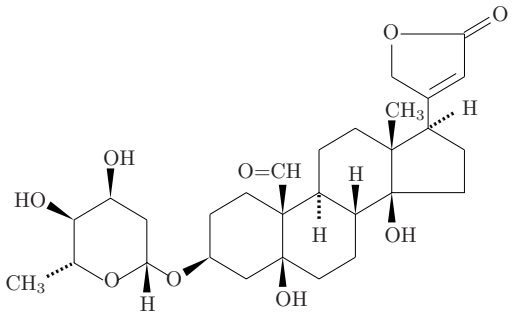
```
¥steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==¥rput(-30,50){O=CH};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GB==H;%
{17}A==¥fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
```

17α-strophanthidin

3β,5,14-trihydroxy-19-oxo-5β,17α-card-20(22)-enolide

Strophanthidin is the aglycon of corchoroside A, whose formula is drawn by using `steroid`. The sugar molecule joined to the 3-OH of strophanthidin can be drawn by using a nested `¥lyl` command so as to complete the formula of corchoroside A as follows:

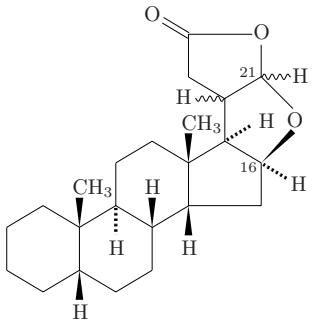
corchoroside A



```
¥begin{XyMcompd}(2200,1400)(-650,150){}{}
¥steroid{%
3B==¥lyl(3==O){3==¥sixheterovi{1==O}{%
2==(yl);
2GB==H;4B==OH;6A==CH$_{3}$;5B==HO}};%
5B==OH;8B==H;9A==H;%
{10}B==¥rput(-30,50){O=CH};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
¥end{XyMcompd}
```

The oxygen-linkage between C-16 and C-21 of 5β-cardanolide generates another five-membered ring. Although a straight-forward method for drawing such an additional ring is unavailable, the formula can be drawn by means of a dirty technique as follows:

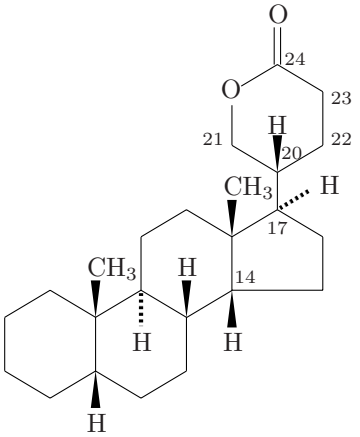
16β,21ξ-epoxy-5β,20ξ-cardanolide



```
¥begin{XyMcompd}(1300,1400)(250,150){}{}
¥steroid[{r{¥sixfusev[%
{f{¥fivefusev{3==O}{4D==O;2SU==H}{a}}}]
{1s==¥psline[unit=0.1pt,linewidth=0.4pt]%
(0,0)(150,-150);%
4s==¥WedgeAsSubst(0,0)(1,1){150};%
1s==¥rput(160,-203){O}
}{6SU==H}{d}[abc]}}]
{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

4.2 Bufanolides

Bufanolides belong to the squill-toad poison group of lactones, where the configurations of 14β and 20R are implied in the name. The lactone moiety can be drawn by using the command `¥sixheterov` in the subslist of the command `¥steroid`.

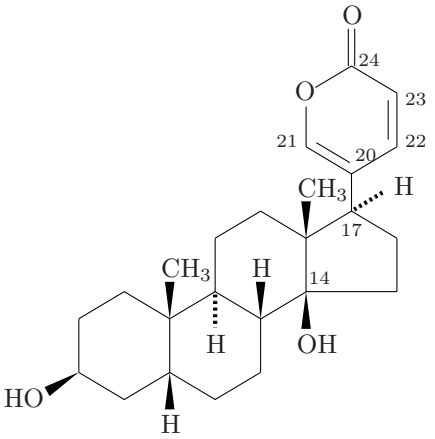


5β-bufanolide

```
¥begin{XyMcompd}(1200,1600)(250,150){}{}
¥steroid{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;%
{{17}}==¥sixheterovi{5==O;%
1s==¥WedgeAsSubst(0,0)(0,1){140};%
1s==¥rput(0,180){H}}{1==(yl);4D==O}}
¥end{XyMcompd}
```

Unsaturated derivatives with two double bonds are named by replacing the suffix -adienolide. In the IUPAC name of the following compound (trivial name: bufalin), the configurations of the two hydroxyl

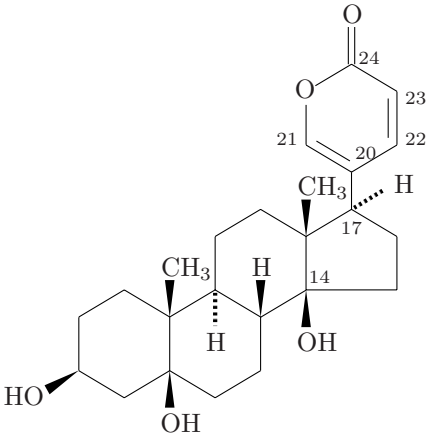
groups are differently specified, i.e., 3β-hydroxy (an explicit specification) and 14-hydroxy (an implicit specification in the name "bufadienolide").



3β,14-dihydroxy-5β-bufa-20,22-dienolide
bufalin

```
¥begin{XyMcompd}(1400,1600)(50,150){}{}
¥steroid{%
3B==HO;5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
¥end{XyMcompd}
```

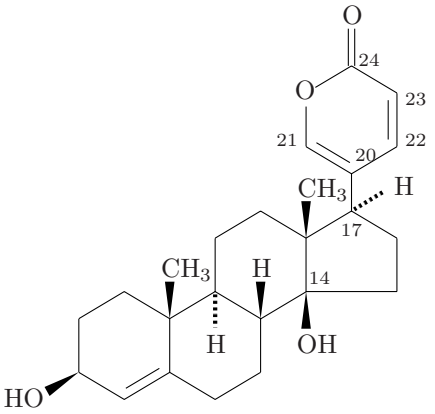
In the IUPAC name of the following compound (trivial name: telecinobufagin), the configurations of the three hydroxyl groups are differently specified, i.e., 3β-hydroxy (an explicit specification), 5-hydroxy (an indirect specification as shown in 5β-bufadienolide), and 14-hydroxy (an implicit specification in the name "bufadienolide").



3β,5,14-trihydroxy-5β-bufa-20,22-dienolide
telecinobufagin

```
¥begin{XyMcompd}(1400,1600)(50,150){}{}
¥steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
¥end{XyMcompd}
```

Unsaturated derivatives with three double bonds are named by replacing the suffix -atrienolide.



3β,14-dihydroxybufa-4,20,22-trienolide
scillarenin

```
¥begin{XyMcompd}(1400,1600)(50,150){}{}
¥steroid[d]{%
3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==¥sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
¥end{XyMcompd}
```

Chapter 5

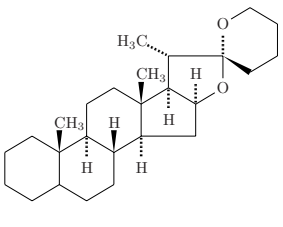
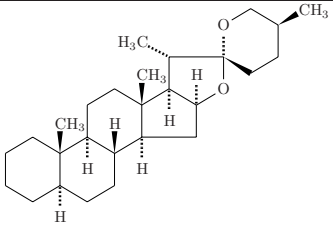
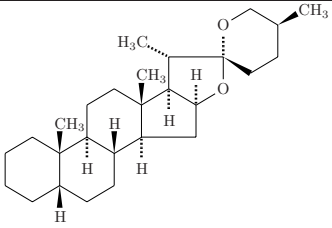
Steroids with Spiro and Fused Heterocycles

5.1 Spirostans

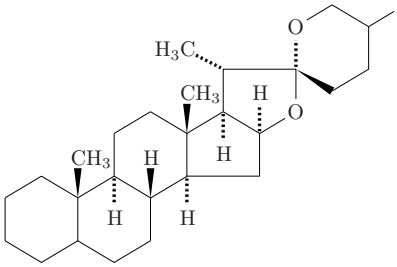
5.1.1 Flat Spiro Rings

In one stereochemical convention, spiro junction in spirostans is expressed by a flat formula (a projection on to the plane of the paper) using a wedged bond and a dashed-line bond. Such flat formulas are supported by the commands listed in Table 5.1.

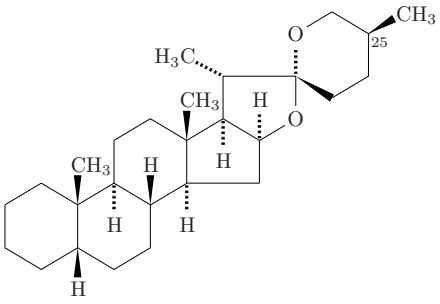
Table 5.1: Spirostans

5 unspecified (nor)	5α series	5β series
		
`¥spirostannor{}`	`¥spirostanalpha{}` 5α-spirostan	`¥spirostanbeta{}` 5β-spirostan

The command `spirostan` is used to draw a spirostan with an unspecified configuration of the 25-methyl group. To draw a 25S-derivative, we overwrite a wedged bond at the C-25 by using the subslist of the `¥spirostan`.

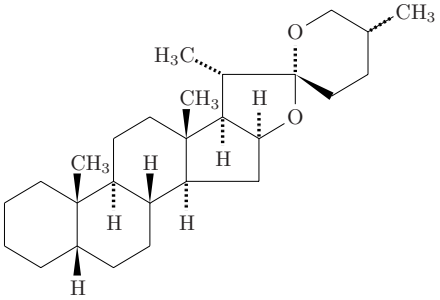


¥spirostan{}
a spirostan

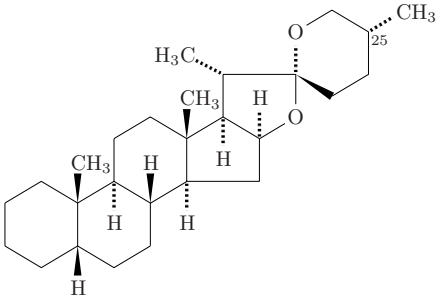


¥spirostan{5B==H;{25}B==CH$_{3}$}
(25S)-5β-spirostan

For the purpose of drawing a 25R-derivative, the overwriting method using ¥spirostan gives an insufficient result, as shown in the first formula below. Instead, we use the command ¥spirostannor to obtain a more acceptable formula, as shown in the second formula below.

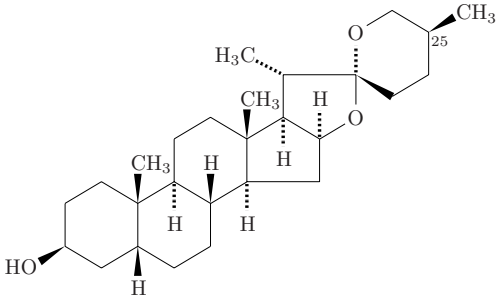


¥spirostan{5B==H;{25}A==CH$_{3}$}
(25R)-5β-spirostan (insufficient)



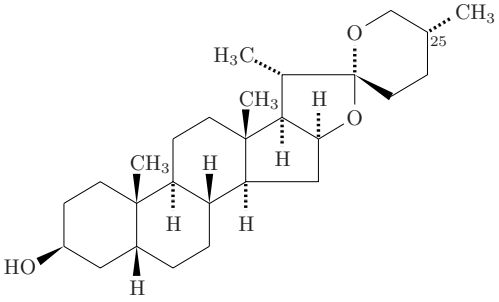
¥spirostannor{5B==H;{25}A==CH$_{3}$}
(25R)-5β-spirostan

Epimerization at the C-25 results in the formation of 25S and 25R stereoisomers of 5β-spirostan-3β-ol. They are differentiated by the prefixes 25S and 25R, as follows:



¥spirostannor{3B==HO;5B==H;
{25}B==CH$_{3}$}

(25S)-5β-spirostan-3β-ol
sarsasapogenin

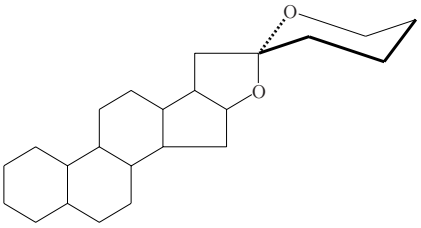


¥spirostannor{3B==HO;5B==H;
{25}A==CH$_{3}$}

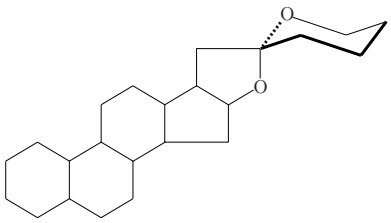
(25R)-5β-spirostan-3β-ol

5.1.2 Chair-Form Spiro Rings

In another stereochemical convention, the spiro pyran ring is expressed as a chair form, which is perpendicular to the plane paper. To draw such an expression, we use the command ¥pyranoseChairi as follows.



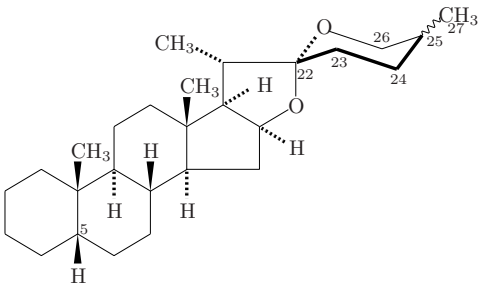
```
¥begin{XyMcompd}(2200,1150)(200,250){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥pyranoseChairi{1==(yl)}}{}{e}%
}}]{}
¥end{XyMcompd}
```



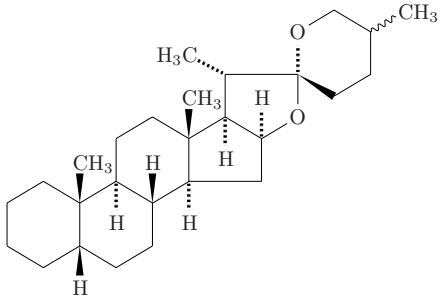
```
¥begin{XyMcompd}(2000,1100)(200,250){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}%
¥pyranoseChairi{1==(yl)}}}{}{e}%
}}]{}
¥end{XyMcompd}
```

The size of the pyran ring can be reduced by using `¥changeunitlength`, as exemplified by the second formula depicted above. It is safe to use the command `¥mbox`, so that the change of a unit length by `¥changeunitlength` is limited to the argument of `¥mbox`.

Because the name spirostan specifies the configurations shown for all the asymmetric centers except positions 5 and 25, the prefix 5α- and 5β is added to specify the configuration of the C-5 according to steroid convention, while 25R or 25S is added to specify the configuration of C-25 according to the sequence-rule procedure. The following formulas illustrate two different expressions of (25ξ)-5β-spirostan, where the configuration of C-25 is not determined, as shown by a wavy line in each expression and by the prefix 25ξ in the name.



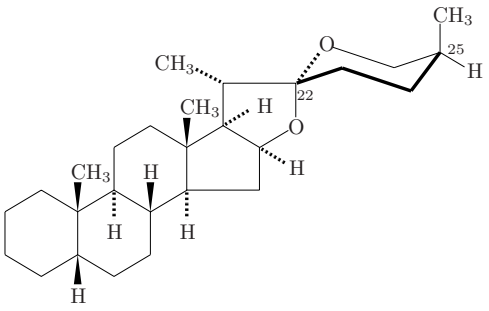
```
¥begin{XyMcompd}(2200,1350)(200,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.07pt}%
¥pyranoseChairi{1==(yl);%
4U=={¥normalsize CH$_{3}$}}}}
{4A==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```



```
¥spirostannor{5B==H;{25}U==CH$_{3}$}
```

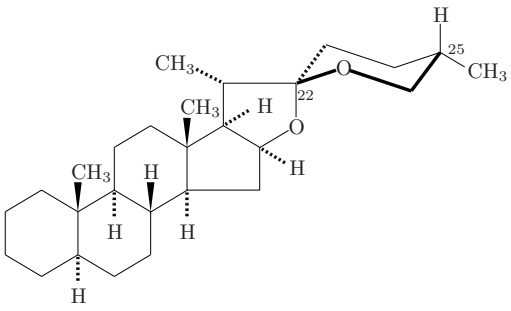
(25ξ)-5β-spirostan

A fixed configuration at the C-25 atom of the spirostan skeleton is depicted as follows by using the subslist of the command `¥pyranoseChairi` or `¥pyranoseChairii`, which is defined in a similar way to the command `chairi` for drawing chair-form derivatives of cyclohexane.



```
¥begin{XyMcompd}(2200,1350)(200,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}%
¥pyranoseChairi{1==(yl);%
4Sa=={¥normalsize CH$_{3}$};%
4Se=={¥normalsize H}}}}{4A==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

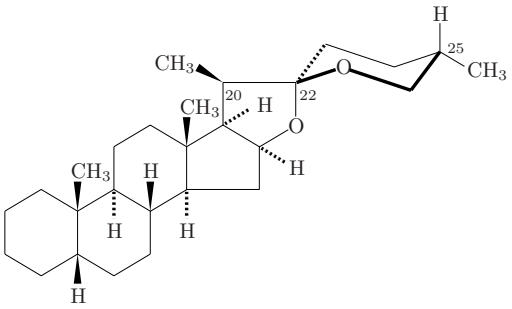
$(25S)$-5β-spirostan



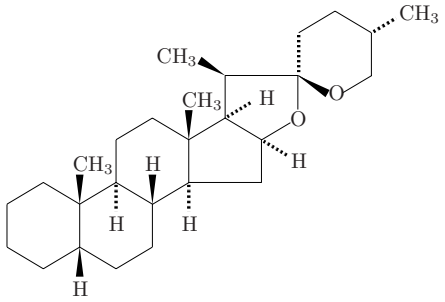
```
¥begin{XyMcompd}(2200,1350)(200,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}%
¥pyranoseChairii{1==(yl);%
4Se=={¥normalsize CH$_{3}$};%
4Sa=={¥normalsize H}}}}{4A==CH$_{3}$}{e}%
}}]{5A==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

$(22R,25S)$-5α-spirostan

The following formulas of cyclopseudoneogenin (flat and chair-form types) show a stereoisomer of $(22R,25S)$-5α-spirostan depicted above, where the configurations of C-5 and C-20 are inverted. The prefix $(20R,22S,25S)$ of the systematic name contains the specification of the configuration at the C-20, which is different from the implicit configuration of the name spirostan.



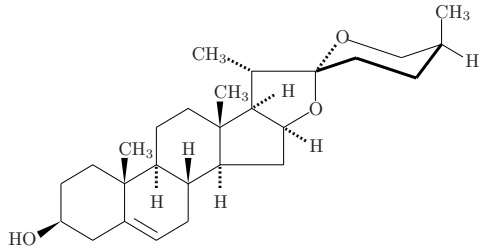
```
¥begin{XyMcompd}(2200,1350)(250,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}%
¥pyranoseChairii{1==(yl);%
4Se=={¥normalsize CH$_{3}$};%
4Sa=={¥normalsize H}}}}{4B==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

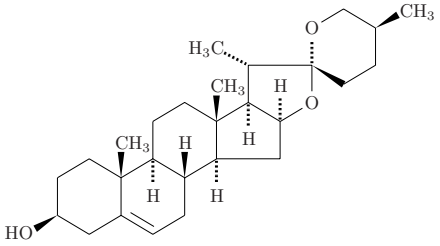


```
¥begin{XyMcompd}(1900,1350)(250,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥sixheterovi({eA}){%
1==O;
6s==¥WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3A==CH$_{3}$}
}{4B==CH$_{3}$}{e}}}]
{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

$(20R,22S,25S)$-5β-spirostan (trivial name: cyclopseudoneogenin)

Yamogenin ((25S)-spirost-5-en-3β-ol), an aglycon of a saponin extracted from yams (Yamanoimo), is shown below, where structural formulas of two types for yamogenin are drawn.





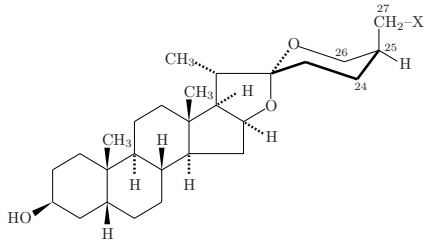
```
¥begin{XyMcompd}(2350,1350)(50,150){}{}
¥steroid[e%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}%
¥pyranoseChairi{1==(yl);%
4Sa=={¥normalsize CH$_{3}$};%
4Se=={¥normalsize H}}}}{4A==CH$_{3}$}{e}%
}}]{3B==HO;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

```
¥begin{XyMcompd}(2100,1350)(50,150){}{}
¥spirostannor[e]{3B==HO;{25}B==CH$_{3}$}
¥end{XyMcompd}
```

(25S)-spirost-5-en-3β-ol (trivial name: yamogenin)

Formulas of two types for diosgenin ((25R)-spirost-5-en-3β-ol), which is the C-25 epimer of yamogenin, can be drawn similarly by exchanging `4Sa` and `4Sb` in the first program and by placing `{25}A==CH$_{3}$` in place of `{25}B==CH$_{3}$` of the second program.

RS-Stereodescriptors for configurations at the C-25 of spirostans are influenced by substituents around the C-25 atoms, even if the carbon skeletons around the C-25 are unchanged to give fixed configurations. The following three compounds are typical examples, where their *RS*-stereodescriptors varies in accord with the priority sequences, although their configurations at the C-25 are chemically unchanged.



X = H: 25S
26(OHH) > 24(CHH) > 27(HHH) > H
(25S)-5β-spirostan-3β-ol (sarsasapogenin)

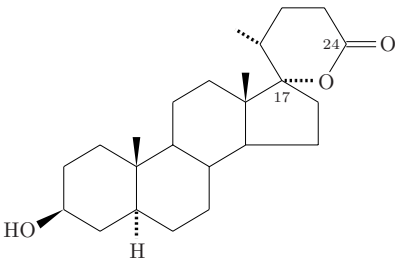
X = OH: 25R
26(O(C)HH) > 27(O(H)HH) > 24(CHH) > H
(25R)-5β-spirostan-3β,27-diol

X = Br: 25S
27(BrHH) > 26(OHH) > 24(CHH) > H
(25S)-27-bromo-5β-spirostan-3β-ol

```
¥begin{XyMcompd}(2350,1350)(50,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥mbox{¥changeunitlength{0.08pt}¥pyranoseChairi{1==(yl);%
4Sa=={¥normalsize CH$_{2}$--X};%
4Se=={¥normalsize H}}}}{4A==CH$_{3}$}{e}%
}}]{3B==HO;5B==H;{10}B==CH$_{3}$;8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

5.2 Spiro Lactone Rings Other Than Spirostans

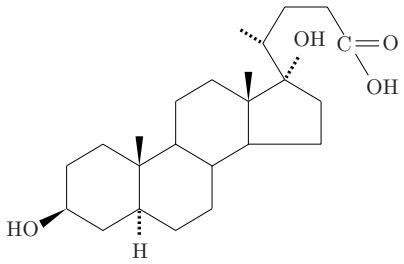
Steroids with a spiro lactone function, other than spirostans, can be drawn by putting a command for a spiro ring in the optional bondlist of such a command as `¥steroid`, where a (yl) function is used.



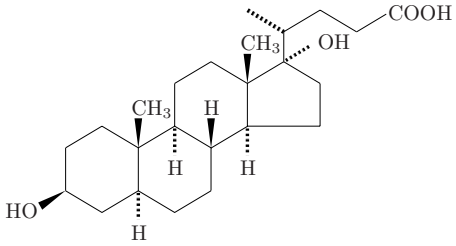
3β-hydroxy-5α-cholano-24,17-lactone

```
¥begin{XyMcompd}(1700,1150)(0,150){}{}
¥steroid[%
{s{¥sixheteroh({eA}){5==O}
{6==(yl);4D==O;1Sd==¥null}}}]
{5A==H;3B==HO;{10}B==¥null;%
{13}B==¥null}
¥end{XyMcompd}
```

The name 3β-hydroxy-5α-cholano-24,17-lactone is based on the corresponding hydroxy-carboxylic acid, which can, for example, be drawn in the following two ways. Thus the name of the lactone contains the locant 24 of the acid group and the locant of the 17-hydroxyl group, where the lactonized hydroxyl group is not explicitly stated.



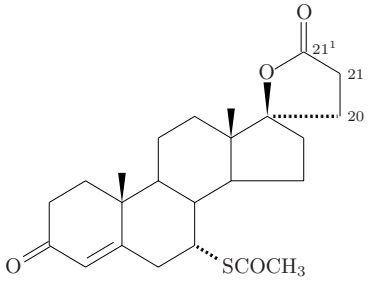

```
¥begin{XyMcompd}(1700,1150)(0,150){}{}
¥steroid[{s{¥sixheteroh
{4==C}{6==(yl);4D==O;4G==OH;%
1Sd==¥null}[de]}}]
{5A==H;3B==HO;{10}B==¥null;%
{13}B==¥null;{17}SA==OH}
¥end{XyMcompd}
```




```
¥begin{XyMcompd}(1900,1150)(0,150){}{}
¥androstanealpha
{3B==HO;{17}GA==OH;%
{17}S==¥rput(-40,24){¥trimethylene%
{1s==¥psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1.2pt]%
(-0,0)(-171,103)%
}{1==(yl);3W==COOH}}}
¥end{XyMcompd}
```

3β,17α-dihydroxy-5β-cholan-24-oic acid

Because a steroid skeleton with a short side chain up to C-21 is named pregnane, a derivative having a carboxylic acid group at the C-21 is called a pregnane-21-carboxylic acid. The following lactone is named as a lactone of such a pregnane-21-carboxylic acid, where the linkage between the C-21 and the C-17 is brought about by the unit -COO- in the lactone ring.



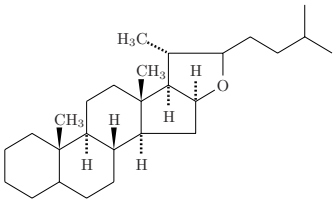
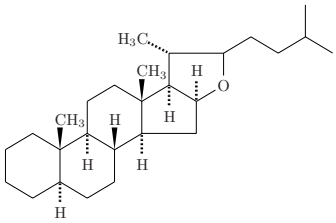
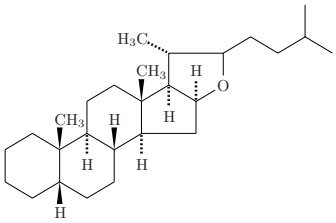
7α-acetylthio-3-oxo-17α-pregn-4-ene-21,17-carbolactone
(internationally non-proprietary name: spironolactone)

```
¥begin{XyMcompd}(1550,1250)(50,200){}{}
¥steroid[d%
{s{¥fiveheterovi({cA})[%
{d{¥WedgeAsSubst(0,0)(0,1){160}}}]
{5==O}
{4==(yl);1D==O}[d]}}]
{3D==O;{10}B==¥null;%
{13}B==¥null;7A==SCOCH$_{3}$}
¥end{XyMcompd}
```

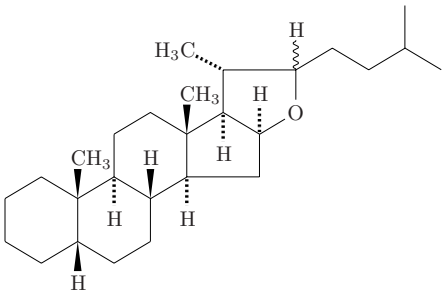
5.3 Furostans

Furostans are steroids with a fused furan ring. Commands for drawing furostans are listed in Table 5.2. The configurations of the C-5 (α or β) and the C-22 (R, S, or ξ) as well as the C-25 (R, S, or ξ if necessary) should be specified afterwards in the prefix of a systematic name, while all of the remaining asymmetric centers are implicitly involved in the name furostan. In particular, note that the configuration of 20S is implied by the name furostan.

Table 5.2: Furostans

5 unspecified	5α series	5β series
		
`¥furostan{}`	`¥furostanalpha{}` 5α-furostan	`¥furostanbeta{}` 5β-furostan

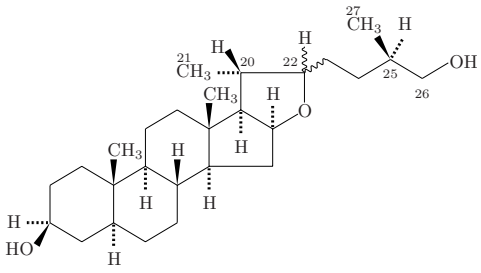
The structural formula of (22ξ)-5β-furostan is easily drawn by using `¥furostanbeta`, where the descriptor `{22}U==H` outputs a wavy bond of a 22ξ-hydrogen, whose configuration is unspecified.



(22ξ)-5β-furostan

```
¥begin{XyMcompd}(1900,1250)(300,200){}{}
¥furostanbeta{{22}U==H}
¥end{XyMcompd}
```

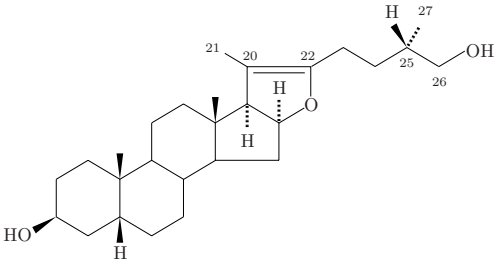
It should be noted that the side chain drawn by `¥furostanbeta` is linked to C-22 through a straight-lined bond while the the hydrogen at the C-22 is linked through a wavy bond. If both of the bonds are desired to be drawn as wavy bonds, the command `¥tetramethylene` is used with `3U` (a designator for a wavy bond) in the subslist of the command `¥fivefusev`, as shown in the following example:



(22ξ,25R)-5α-furostan-3β,26-diol
dihydropseudotigogenin

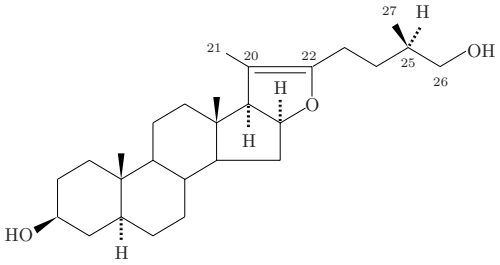
```
¥begin{XyMcompd}(2400,1300)(50,150){}{}
¥steroid[{s{¥fivefusev{2==O}
{4SA==CH$_{3}$;4SB==H;5FA==H;3FU==H;%
3U==¥tetramethylenei{}{1==(yl);%
3SB==CH$_{3}$;3SA==H;4W==OH}}{e}}}]
{3SB==HO;3SA==H;5A==H;%
8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;%
{20}S==CH$_{3}$;{16}FA==H}
¥end{XyMcompd}
```

The first formula below requires a more complicated combination of commands such as `¥steroid`, `fivefusev`, and `¥pentamethylene`. The trivial name pseudosarsasopgenin indicates the relationship to sarsasapogenin, which is a synonym of (25*S*)-5β-spirostan-3β−ol. The second formula below, which is a diastereomer of the first one, can be drawn in a similar way. The trivial name pseudotigogenin indicates the relationship to tigogenin, which is a synonym of (25*R*)-5α-spirostan-3β−ol.




```
¥begin{XyMcompd}(2400,1300)(50,150){}{}
¥steroid[{s{¥fivefusev[c]{2==O;%
3s==¥pentamethylene{}{1==(yl);%
4SA==¥null;4SB==H;5W==OH}
}{4==¥null;5FA==H}{e}}}]
{3B==HO;5B==H;%
{10}B==¥null;%
{13}B==¥null;%
{20}S==¥null;{16}FA==H}
¥end{XyMcompd}
```

(25*S*)-5β-furost-20(22)-en-3β,26-diol
pseudosarsasapogenin



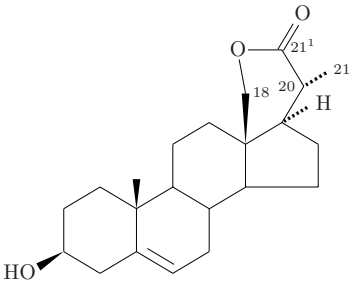

```
¥begin{XyMcompd}(2400,1300)(50,150){}{}
¥steroid[{s{¥fivefusev[c]{2==O;%
3s==¥pentamethylene{}{1==(yl);%
4SB==¥null;4SA==H;5W==OH}
}{4==¥null;5FA==H}{e}}}]
{3B==HO;5A==H;%
{10}B==¥null;%
{13}B==¥null;%
{20}S==¥null;{16}FA==H}
¥end{XyMcompd}
```

(25*R*)-5α-furost-20(22)-en-3β,26-diol
pseudotigogenin

5.4 Fused Lactone Rings Other Than Furostans

A derivative having a carboxylic acid group at the C-21 is regarded a pregnane-21-carboxylic acid. The following lactone is named as a lactone of such a pregnane-21-carboxylic acid, where the linkage between the C-21 and the C-18 is brought about by the unit -COO- in the lactone ring.

(20*R*)-3β-hydroxypregn-5-ene-20,18-carbolactone



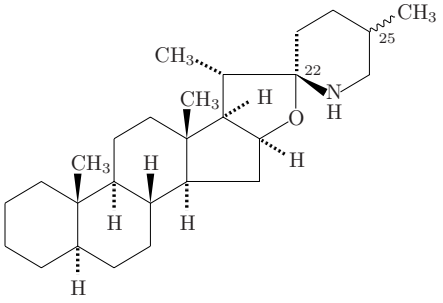

```
¥begin{XyMcompd}(1400,1250)(0,250){}{}
¥steroid[e%
{s{¥sixheteroh{2==O}{5==(yl);3D==O;4Sd==¥null}%
[aef]}}
{o{¥WedgeAsSubst(0,0)(0,1){240}}}%
{o{¥psline[unit=0.1pt,linewidth=0.4pt]%
(0,240)(-30,400)}}]
{3B==HO;{10}B==¥null;{17}GA==H}
¥end{XyMcompd}
```

5.5 Steroid Alkaloids

5.5.1 Spirosolanes

The structural formula of spirosolane is drawn in a similar way to spirostan. Because the bond between N and H is not drawn usually, the command `¥downnobond` is used to place N and H up and down without a bond. The name spirosolane does not imply the configurations at the C-22 and C-25 (in addition to C-5) so that these are explicitly specified by the prefixes. The other asymmetric centers are implied in the name spirosolane.

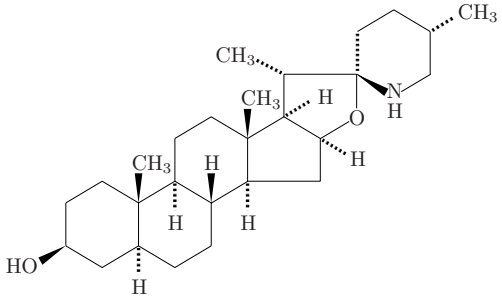
$(22S,25\xi)$-5α-spirosolane



```
¥begin{XyMcompd}(1850,1350)(300,150){}{}
¥steroid[{s{¥fivefusev{2==O;%
3s==¥sixheterovi({eA}){%
1==¥downnobond{N}{H};%
6s==¥WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3U==CH$_{3}$}
}{4A==CH$_{3}$}{e}}}]
{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

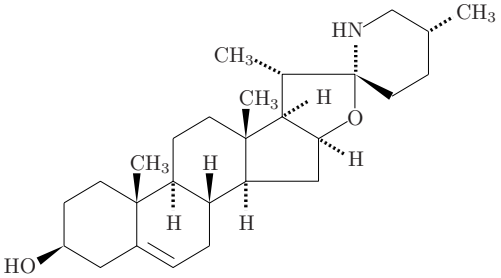
The name tomatanine has been used in place of spirostan. According to this convention, the above compound is named $(22S,25\xi)$-5α-tomatanine.

Tomatidine and solasodine are systematically named as spirosolane derivatives, where the configurations of C-22, C-25 and C-5 are explicitly specified in addition to the configuration of a newly introduced C-3 substituent. The drawing of their structural formulas is straightforward after the above code for the spirosolane skeleton is available. What we have to do is the specification of double bonds and substituents as follows:



```
¥begin{XyMcompd}(2150,1350)(0,150){}{}
¥steroid[%
{s{¥fivefusev{2==O;%
3s==¥sixheterovi({eA}){%
1==¥downnobond{N}{H};
6s==¥WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3A==CH$_{3}$}
}{4A==CH$_{3}$}{e}}}]
{3B==HO;5A==H;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

$(22S,25S)$-5α-spirosolan-3β-ol
tomatidine



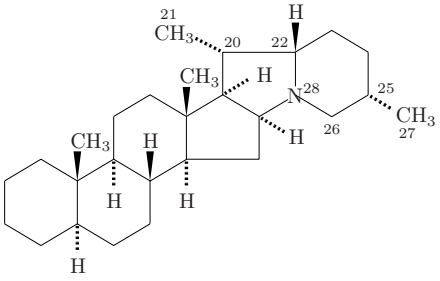
```
¥begin{XyMcompd}(2150,1350)(0,150){}{}
¥steroid[e%
{s{¥fivefusev{2==O;%
3s==¥sixheterovi({eA}){5==¥lmoiety{HN};%
6s==¥WedgeAsSubst(0,0)(5,-3){171}%
}{6==(yl);3A==CH$_{3}$}[f]%
}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

$(22R,25R)$-spirosol-5-en-3β-ol
solasodine

5.5.2 Solanidanines

The parent skeleton named solanidanine (CAS name: solanidane) is drawn by `¥steroid` in combination with nested commands `¥fivefusev` and `¥sixfusev`. The stereodescriptors 22S and 25S for the following compound should be described in the prefix of the systematic name. Note that 16αH, 17αH, and 20S (in addition to usual implicit locants of a steroid skeleton) is implied by the name solanidanine or solanidenine.

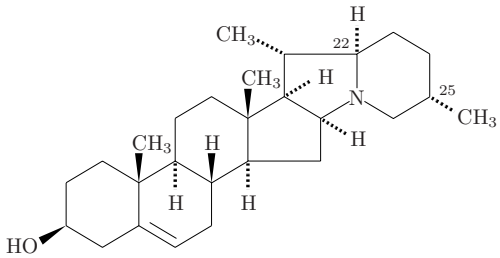
(22*S*, 25*S*)-5α-solanidanine



```
¥begin{XyMcompd}(1900,1150)(250,250){}{}
¥steroid[%
{s{¥fivefusev[%
{b{¥sixfusev{5==N}{3A==CH$_{3}$;6GB==H}{e}}}]
{2==¥null}{4A==CH$_{3}$}{e}}}]
{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

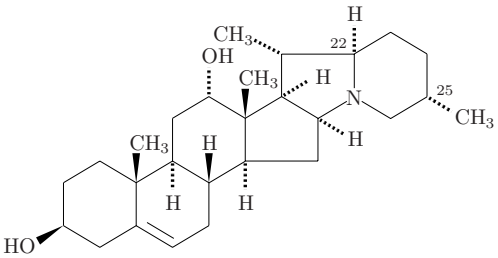
For the purpose of obtaining a systematic name for a solanidanine derivative having a double bond, the end -anine is replaced by -enine to give solanidenine as the name of the skeleton. An additional set of substituents is represented usually as exemplified in the following compound.

(22*R*, 25*S*)-solanid-5-enin-3β-ol
solanidine



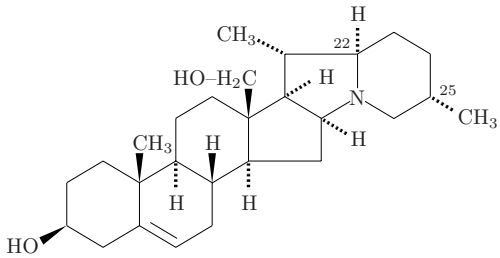
```
¥begin{XyMcompd}(2100,1150)(50,250){}{}
¥steroid[e%
{s{¥fivefusev[
{b{¥sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==¥null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

The structural formulas of rubijervine and isorubijervine can be drawn in a similar way, where the respective subslists of `¥steroid` are slightly modified.



```
¥begin{XyMcompd}(2100,1150)(50,250){}{}
¥steroid[e%
{s{¥fivefusev[
{b{¥sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==¥null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{12}A==OH;{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

(22*R*, 25*S*)-solanid-5-enine-3β,12α-diol
rubijervine

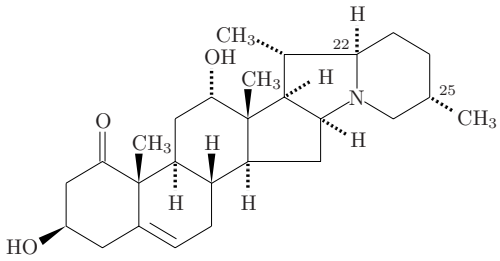


```
¥begin{XyMcompd}(2100,1150)(50,250){}{}
¥steroid[e%
{s{¥fivefusev[
{b{¥sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==¥null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==¥lmoiety{HO--H$_{2}$C};{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

(22*R*, 25*S*)-solanid-5-enine-3β,18-diol
isorubijervine

The following compound can be regarded as the 1-oxo derivative of rubijervine, so that only the code `1D==O` is added to the subslist of `¥steroid` in the abovementioned program for drawing rubijervine.

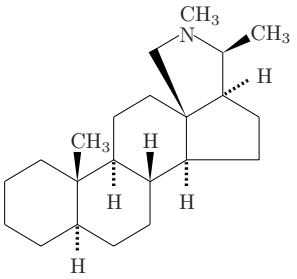
(22R, 25S)-3β,12α-dihydroxysolanid-5-enin-1-one




```
¥begin{XyMcompd}(2100,1150)(50,250){}{}
¥steroid[e%
{s{¥fivefusev[
{b{¥sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==¥null}{4A==CH$_{3}$}{e}}}]
{1D==O;3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{12}A==OH;{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
¥end{XyMcompd}
```

5.5.3 Conanines

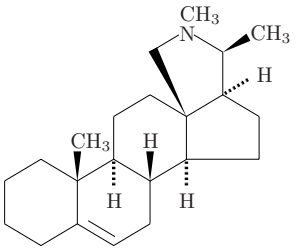
The name conanine implies 17αH and 2OS in addition to the other asymmetric centers of the steroid skeleton. The formula of 5α-conanine is drawn as follows:



5α-conanine

```
¥begin{XyMcompd}(1200,1200)(250,150){}{}
¥steroid[{T{¥sixfusev
{4s==¥WedgeAsSubst(0,0)(-1,2){158};%
1==¥upnobond{N}{CH$_{3}$}
}{2B==CH$_{3}$}{c}[de]}}]
{5A==H;8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;{17}GA==H}
¥end{XyMcompd}
```

The introduction of a double bond between C-5 and C-6 gives con-5-enine, whose structure is drawn as follows:



con-5-enine

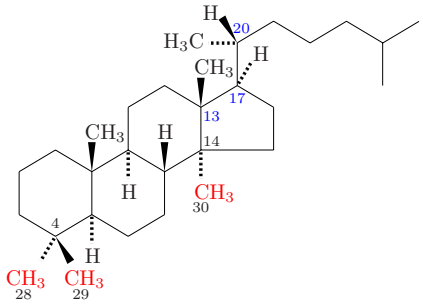
```
¥begin{XyMcompd}(1200,1200)(250,150){}{}
¥steroid[e{T{¥sixfusev
{4s==¥WedgeAsSubst(0,0)(-1,2){158};%
1==¥upnobond{N}{CH$_{3}$}
}{2B==CH$_{3}$}{c}[de]}}]
{8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;{17}GA==H}
¥end{XyMcompd}
```

Chapter 6

Tetracyclic Triterpenoids Related to Steroids

6.1 Lanostanes

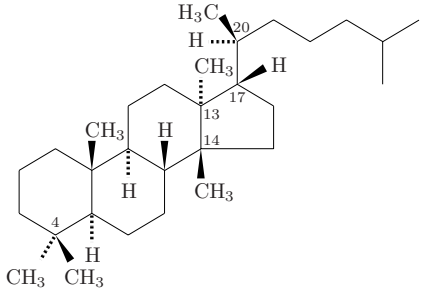
Tetracyclic triterpenoids can be regarded as 4,4,14-trimethyl-substituted steroids, where the methyl groups at 4α and 4β are numbered as C-28 and C-29 respectively, while the methyl group at the 14-position is specified by the locant 30. For example, 5α-lanostane represents a compound which is designated by a systematic name 4,4,14α-trimethyl-5α-cholestane. The configurations of 14α- and 20R (in addition of the other configurations specified by the steroid convention, e.g., 13β and 17β) are implied by the name 5α-lanostane, when this is used as a parent molecule in the process of naming further derivatives. The formula of 5α-lanostane is drawn by using the command `¥steroidChain`.



5α-lanostane
4,4,14α-trimethyl-5α-cholestane

```
¥steroidChain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==CH$_{3}$;%
{17}SA==¥raisebox{-4pt}{˜H};%
{20}SA==H$_{3}$C;{20}SB==H}
```

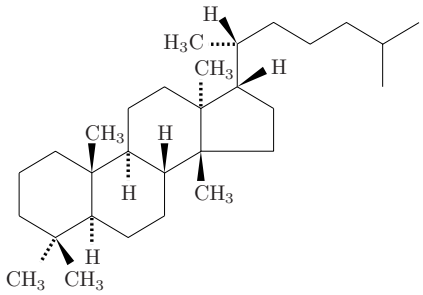
The trivial name 5α-tirucallane is used widely. Because the configurations at the C-20, C-13, C-14, and C-17 are inverted in comparison with the implied 20R etc. of the parent lanostane, the prefix of the following systematic name contains the descriptors 20S etc.



5α-tirucallane
(20S)-5α,13α,14β,17α-lanostane

```
¥steroidChain
{4Su==CH$_{3}$;4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}A==CH$_{3}$;{14}B==CH$_{3}$;%
{17}GB==H;{20}SB==H$_{3}$C;{20}SA==H}
```

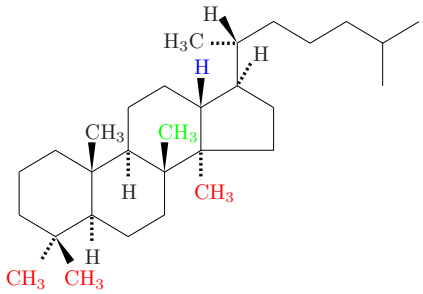
The trivial name 5α-euphane is widely used. The name lanostane for the systematic name implies 20R, which needs not be specified in the prefix of the following name.



5α-euphane
5α,13α,14β,17α-lanostane

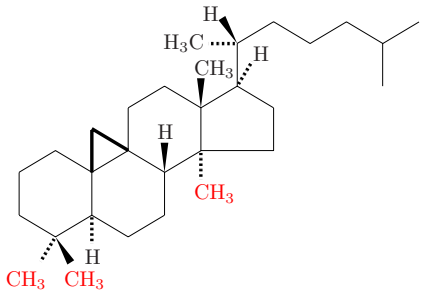
```
¥steroidChain
{4Su==CH$_{3}$;4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}A==CH$_{3}$;{14}B==CH$_{3}$;%
{17}GB==H;{20}SA==H$_{3}$C;{20}SB==H}
```

The structural formulas of dammarane, cycloartane, and protostane can be drawn in a similar way by using `steroidChain`.



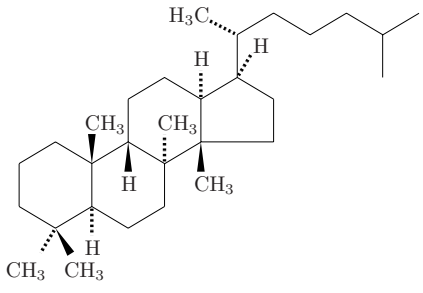
dammarane
8-methyl-18-nor-5α-lanostane
4,4,8,14-tetramethyl-18-nor-5α-cholestane

```
¥steroidChain{4Su=={¥red CH$_{3}$};%
4Sd==CH$_{3}$;5A==H;%
8B==CH$_{3}$;9A==H;%
{10}B==CH$_{3}$;{13}B==H;%
{14}A==CH$_{3}$;%
{17}SA==¥raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```



cycloartane
9,19-cyclo-9β-lanostane
4,4,14-trimethyl-9,19-cyclo-5α,9β-cholestane

```
¥steroidChain[{%
I¥threefuseh({bB}{cB}){}{}{a}}]
{4Su==CH$_{3}$;4Sd==CH$_{3}$;%
5A==H;8B==H;{13}B==CH$_{3}$;%
{14}A==CH$_{3}$;%
{17}SA==¥raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```

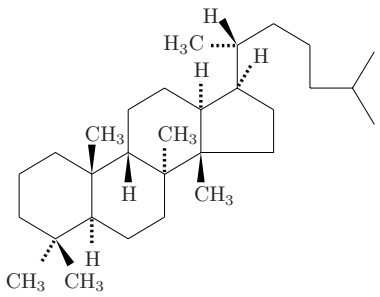


protostane
4,4,8,14-tetramethyl-18-nor-5α,8α,9β,13α,14β-cholestane

```
¥steroidChain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8A==CH$_{3}$;9B==H;%
{10}B==CH$_{3}$;{13}A==H;%
{14}B==CH$_{3}$;%
{17}SA==¥raisebox{-4pt}{~H};%
{20}A==H$_{3}$C}
```

The same compound (protostane) with an alternative folding of the side chain can be drawn by using

`¥steroidchain` in place of `¥steroidChain`, where any modification of the subslist is not necessary. The result is shown below:



6.2 Biosynthesis of Steroids

Lanosterol, a tetracyclic triterpenoid, is an intermediate for the biosynthesis of cholesterol from squalene, as summarized in Fig. 6.1.

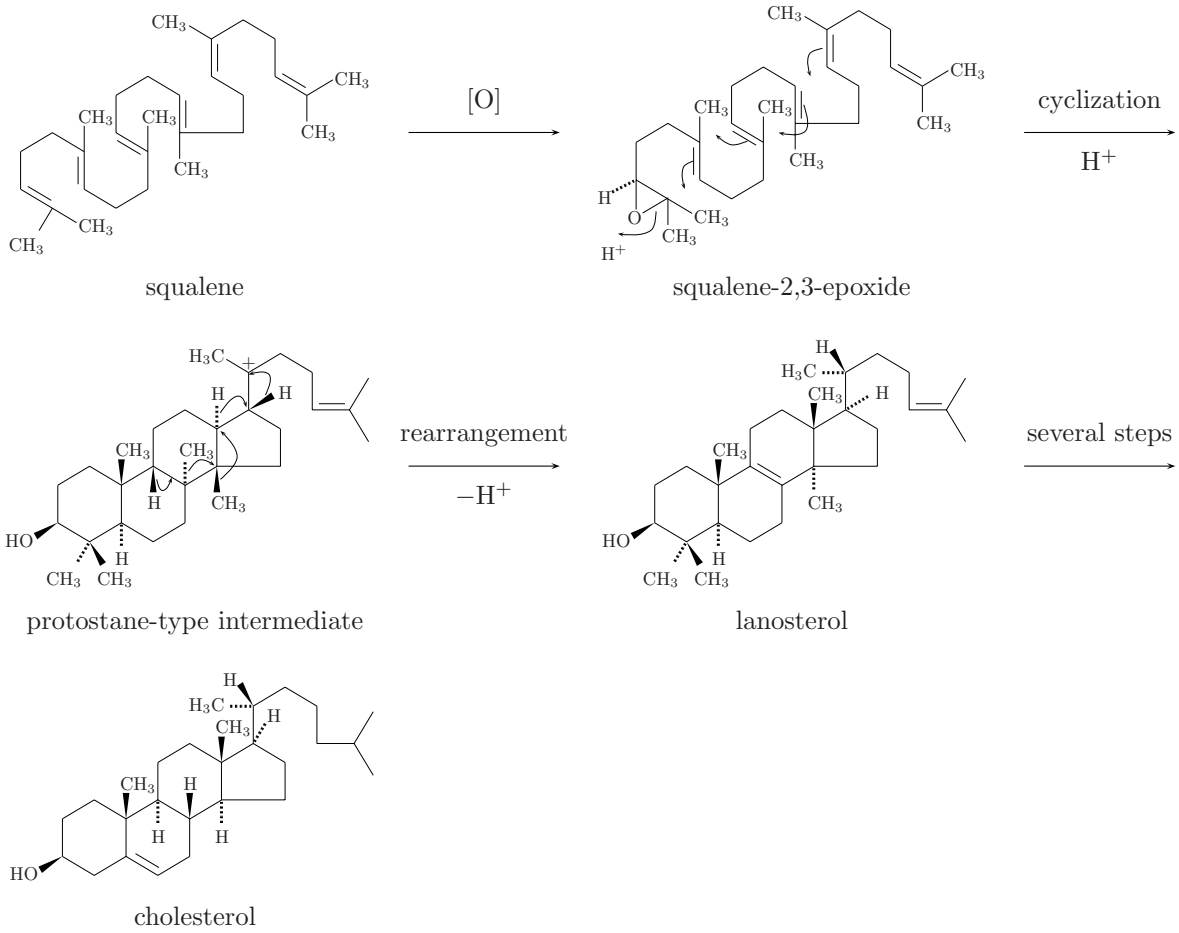


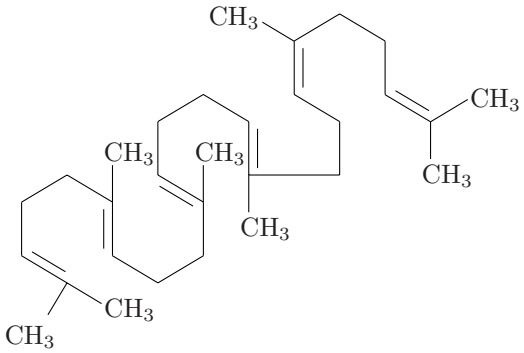
Figure 6.1: Biosynthesis of cholesterol from squalene

To draw the scheme shown in Fig. 6.1, commands for drawing respective compounds are defined by

using the commands supported by the XΥMTEX system. First, the command ¥squalene for drawing the starting compound squalene is defined by the multiple nesting ($6 \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6$) of sixfusev and ¥fivefusevi in the bondlist of ¥sixheterov.

```
¥def¥squalene
{%
¥begin{XyMcompd}(1800,1300)(250,0){}{}
¥sixheterov[bd{B{¥sixfusev[a{A{¥sixfusev[{B{¥fivefusevi[d%
{A{¥sixfusev[e{c{¥dimethylenei[a]{}{1==(yl);2==CH$_{3}$;2W==CH$_{3}$}}}]
{}{6==CH$_{3}$}{d}[c]}}]{}{}{d}[e]}}]{}{3G==CH$_{3}$}{d}[c]}}]
{}{2F==CH$_{3}$}{e}[f]}}]{}{4Sb==CH$_{3}$;4F==CH$_{3}$;2F==CH$_{3}$}[c]
¥end{XyMcompd}
}
```

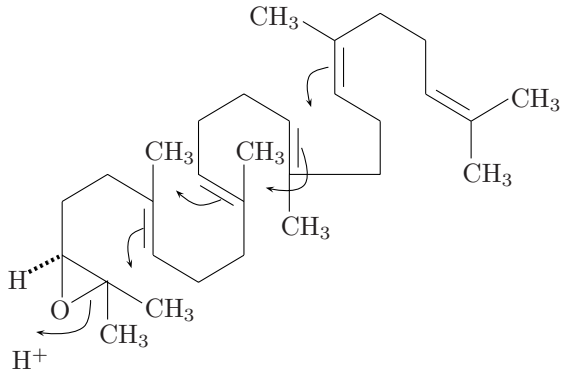
Output of ¥squalene without size reduction:



Second, the command ¥squaleneepoxide is defined for drawing squalene-2,3-epoxide, which contains arrows for representing electron shifts during cyclization. Each of these arrows is drawn by using ¥pscurve of the PStricks package, which is placed in the atomlist of ¥threefuseh, ¥sixfusev, or ¥fivefusevi. Each arrow is drawn from the midpoint of a starting double bond to the midpoint of a single bond to be formed according to a convention of organic chemistry. The epoxide ring is drawn by using ¥threefuseh, so that total multiple nesting is represented by the scheme, $6\ (\leftarrow 3) \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6$.

```
¥def¥squaleneepoxide
{%
¥begin{XyMcompd}(2000,1300)(50,-50){}{}
¥sixheterov[b{D{¥threefuseh{2==O;%
2==¥rput(-150,-150){H$^{+}$};%
2==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-130,-50)(50,-30)(75,70)%
}{}{c}}}%
{B{¥sixfusev[a{A{¥sixfusev[{B{¥fivefusevi[d{A{¥sixfusev[e{c{¥dimethylenei%
[a]{}{1==(yl);2==CH$_{3}$;2W==CH$_{3}$}}}]{%
5s==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-85,-50)(-90,70)(-20,100)%
}{6==CH$_{3}$}{d}[c]}}%
]{%
4s==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-85,-50)(60,-40)(50,100)%
}{}{d}[e]}}%
]{}{3G==CH$_{3}$}{d}[c]}}%
]{%
1s==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-85,-60)(0,-115)(85,-95)%
}{2F==CH$_{3}$}{e}[f]}}]%1
{3s==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-85,-50)(-90,70)(-40,100)%
}{5A==H;4==CH$_{3}$;4F==CH$_{3}$;2F==CH$_{3}$}[c]%3
¥end{XyMcompd}
}
```

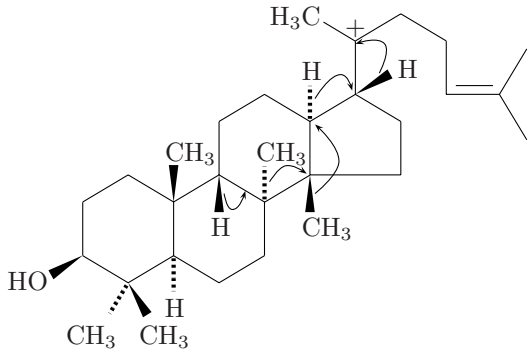
Output of ¥squaleneepoxide without size reduction:



The intermediate of protostane-type is drawn by using ¥protostaneintermediate, which is defined on the basis of steroidchain. This formula contains arrows for representing electron shifts during cyclization. These arrows are drawn by using the ¥pscurve commands, which are placed before a substituent (H or CH_3) in the subslist of ¥steroidchain. This technique is based on the specification of ¥pscurve, which outputs a curved line having no size. According to a convention of organic chemistry, the starting point of each arrow is the midpoint of a cleaved bond, while its end point is the site (atom) at which a new bond is formed or the midpoint of a double bond to be formed.

```
¥def¥protostaneintermediate
{%
¥begin{XyMcompd}(1800,1300)(50,0){}{}
¥steroidchain[{Ze}{s{¥rput(0,250){+}}}]{3B==HO;4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8A==¥pscurve[unit=0.1pt,linewidth=0.4pt]{->}(50,-80)(110,-20)(190,-50)CH$_{3}$;%
9B==¥pscurve[unit=0.1pt,linewidth=0.4pt]{->}(50,160)(80,100)(130,170)H;%
{10}B==CH$_{3}$;%
{13}A==¥pscurve[unit=0.1pt,linewidth=0.4pt]{->}(50,-70)(150,20)(190,-40)H;%
{14}B==¥pscurve[unit=0.1pt,linewidth=0.4pt]{->}(50,160)(140,280)(50,420)CH$_{3}$;%
{17}GB==¥pscurve[unit=0.1pt,linewidth=0.4pt]{<-}(-160,130)(-50,130)(-70,20)H;%
{20}S==H$_{3}$C}
¥end{XyMcompd}
}
```

Output of ¥protostaneintermediate without size reduction:

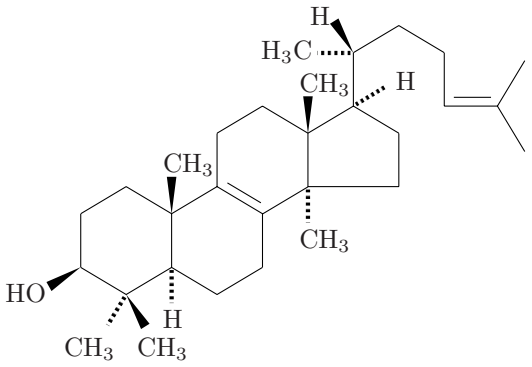


The command ¥lanosterol is defined on the basis of ¥steroidchain.

```
¥def¥lanosterol
{%
```

```
¥begin{XyMcompd}(1800,1300)(50,0){}{}
¥steroidchain[h{Ze}]{3B==HO;4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}A==CH$_{3}$;{17}GA==H;{20}SA==H$_{3}$C;{20}SB==H}
¥end{XyMcompd}
}
```

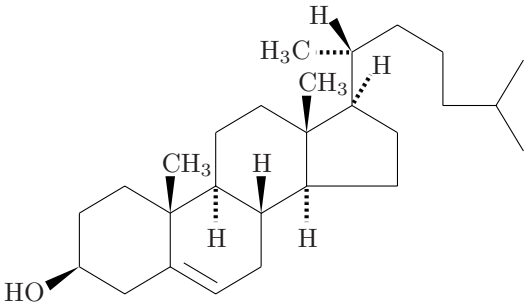
Output of ¥lanosterol without size reduction:



The command ¥cholesterol is defined by a rather straight-forward use of ¥cholestanE, which is supported by the preset version of the XyMTEX system.

```
¥def¥cholesterol
{%
¥begin{XyMcompd}(1750,1100)(50,200){}{}
¥cholestanE[e]{3B==HO}
¥end{XyMcompd}
}
```

Output of ¥cholesterol without size reduction:



Finally, these commands are arranged by using the LaTeX 2ε tabular environment, where the size of each formula is reduced by means of ¥scalebox supported by the graphicx package. The command ¥reactrarrow, which is defined in the chemist package loaded by means of ¥usepackage, is used to draw an arrow representing a chemical reaction.

```
¥begin{figure}[h]
¥begin{center}
¥begin{tabular}{cccc}
¥scalebox{0.7}{¥squalene} &
¥reactrarrow{0pt}{2cm}{[O]}{¥strut} &
¥scalebox{0.7}{¥squaleneepoxide} &
¥reactrarrow{0pt}{2cm}{cyclization}{H$^{+}$} ¥¥
```

```
¥noalign{¥vskip5pt}
squalene & & squalene-2,3-epoxide & ¥¥
¥noalign{¥vskip15pt}
¥scalebox{0.7}{¥protostaneintermediate} &
¥reactrarrow{0pt}{2cm}{rearrangement}{$-$H$^{+}$} &
¥scalebox{0.7}{¥lanosterol} &
¥reactrarrow{0pt}{2cm}{several steps}{¥strut} ¥¥
¥noalign{¥vskip5pt}
protostane-type intermediate & & lanosterol & ¥¥
¥noalign{¥vskip15pt}
¥scalebox{0.7}{¥cholesterol} &&& ¥¥
¥noalign{¥vskip5pt}
cholesterol &&&¥¥
¥end{tabular}
¥end{center}
¥caption{Biosynthesis of cholesterol from squalene}
¥label{ff:Biosyntheis}
¥end{figure}
```

The tabulated scheme is incorporated in the `figure` environment of the LaTeX 2_ε system. The output of the scheme is shown in Fig. 6.1.

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