FLASH VACUUM PYROLYSIS OF PLANT STEROIDS: THE IMPACT OF STEROID STRUCTURE ON THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS

Michelle K. Kidder, Phillip F. Britt, and A. C. Buchanan, III

Chemical and Analytical Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

Introduction

The fuel community has become interested in biomass as a source of renewable energy for power generation and for production of liquid fuels and specialty chemicals. However, like its predecessors, i.e., coal and oil, pyrolysis and combustion of biomass can produce polycyclic aromatic hydrocarbons (PAHs), which are precursors to soot.[1,2] Since pyrolysis reactions dominate in oxygen deficient zones during the combustion of solid fuels, a better understanding of the pyrolysis reactions may lead to the ability to control the production of PAHs during the thermochemical processing of biomass.

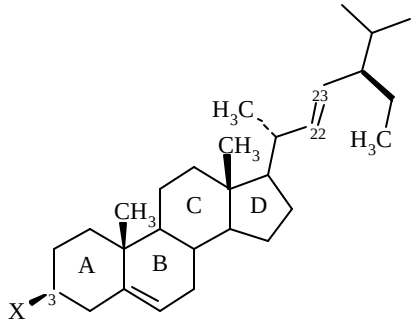
A significant amount of research has focused on the formation of PAHs from the pyrolysis of the major constituents of woody biomass, i.e., cellulose and lignin. However, many of the reaction mechanisms that lead to product formation are unclear due to the numerous competing reaction pathways and the complexity of the pyrolysis tars. To simplify this situation, we have focused on the pyrolysis of biomass model compounds at short residence times (< 1 s), which is more relevant to the current process conditions, i.e. fast pyrolysis.[3,4]

In this investigation, the formation of PAHs from the flash vacuum pyrolysis (FVP) of plant steroids is investigated since the native ring structure of steroids appear to be preorganized for the formation of phenanthrene type PAH structures. These steroids are found as the free sterol and as sterol ester in the plant lipid membrane, and they can be isolated from the nonpolar extract of biomass or from the tall oils produced from the Kraft process.[5] In the dry foliage of Scotch pine, for example, sterol esters are found in 1.1 wt%, which is composed of β-sitosterol (84%), stigmasterol and campesterol.[6] To determine if the native steroid structure can produce PAHs, the FVP of typical plant steroids will be investigated at low pressures where only unimolecular reactions can occur. This technique has also been used to investigate the pyrolysis mechanisms of lignin model compounds.[7,8]

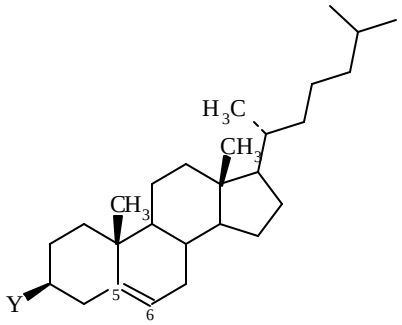
The thermal decomposition of steroids has been previously investigated. Most studies have focused on the hydrous pyrolysis, since isomerization of these biological markers are used as an indication of maturity of sediments. There have only been a few studies on the pyrolysis of steroids at short residence times. The Curie point pyrolyisis of a series of structurally related steroids, including stigmasterol, cholesterol, β-sitosterol, demosterol and campesterol[9] and derivatives of androstane,[10] has been investigated and they were found to have a unique pyrochromatographic "fingerprint". It was discovered that the volatile pyrolysis products, were sensitive to structural and stereochemical variations in the steroid. Therefore, we are also interested in how the PAH yields may be influenced by the steroid structure. Thus the products from the FVP of stigmasterol, stigmasterol acetate, β-sitosterol, cholesterol, cholesteryl acetate, and dihydrocholesterol (see **Figure 1**) at 700 ºC will be investigated to determine if their reaction pathways lead to PAH formation and if the PAH yields are dependent on the steroid structure.

Experimental

Stigmasterol (Acros 93.6% by GC), β-sitosterol (Acros 79.6%, 7.6% stigmastanol, 12.5% campesterol by GC), stigmasterol acetate (Sigma, 93.5%), cholesterol (Acros, 95.5%), cholesteryl acetate (Acros, 97.9%), dihydrocholesterol (Acros, 89.1%), and carbon disulfide (Acros), were used without further purification. Phenethyl acetate (Acros) was purified by vacuum fractional distillation before



Stigmasterol: X=OH
Stigmasterol Acetate: X=CH_3COO
b-Sitosterol: X=OH, C_{22}-C_{23} = CH_2CH_2



Cholesterol: Y=OH
Cholesteryl Acetate: Y=CH_3COO
Dihydrocholesterol: Y=OH, C_5-C_6=CH_2CH_2

Figure 1. Structure of steroids. (a) Stigmasterol, stigmasterol acetate, β-sitosterol. (b) Cholesterol, cholesteryl acetate, dihydrocholesterol.

use (purity 99.0% by GC with phenethyl alcohol as the largest impurity 0.6%). Perdeuterated PAHs (phenanthrene-d_{10} and 1,2-benz[a]anthracene-d_{12}) were obtained from Aldrich Chemical Company.

FVP. The FVP apparatus was based on the design reported by Trahanovsky.[11,12] The experimental procedure used in this study was similar to that previously reported by Britt [8] and is briefly described below. A quartz reaction tube (62.5 cm x 2.5 cm) was packed with short quartz chips (1/4 in. x 6 mm o.d. x 40 cm long) in the center of the tube and held in place by a small plug of quartz wool. The tube

was placed in a Carbolite three-zone furnace (45 cm x 3.8 cm i.d.), and the temperature maintained within ±1ºC of the setpoint over a length of 30 cm (out of the total heated zone of 40 cm). The sample was weighed (typically 200-300 mg) into a sublimation tube and connected horizontally to the end of the quartz tube. At the exit end of the furnace, a liquid nitrogen cooled trap was attached. The system was pumped down to $<10^{-4}$ Torr, which was measured after the cold trap.

To sublime the sample, an aluminum cylinder was wrapped in heating tape and placed around the sublimation tube. The temperature of the aluminum cylinder was monitored by a thermocouple in the cylinder and was maintained at a temperature such that the rate of throughput was 50-100 mg/hr. To prevent the pyrolysis products from condensing between the exit end of the reaction tube and the cold trap, the exposed portion of the tube was wrapped in heating tape and maintained at 125 ºC. The pressure during a reaction was typically $5 \times 10^{-5} - 5 \times 10^{-4}$ Torr. The residence time in the FVP experiments was calculated from the pyrolysis of phenethyl acetate in which the Arrhenius parameters have been reported.[13] At 700 ºC, the residence time was calculated to be 0.120 s, but the residence times of the steroids will be approximately 1.6 fold larger due to their higher molecular weight, i.e., 0.190 s for 700 ºC. (The residence time depends on the molecular velocity of the molecule, which has a square root dependence on temperature and molecular weight $(T/MW)^{1/2}$).[14] When the reaction was complete, the trap was opened, the products were washed out with a high purity carbon disulfide and internal standards (*n*-tetradecane or hexatriacontane, phenanthrene-d_{10}, and benz[a]anthracene-d_{12}) were added. The samples were then analyzed by GC and GC-MS as described below. After each run, the tube was "burned out" by heating the tube to 600 ºC while blowing air through the tube for 1 h, to remove any carbonaceous deposits.

Analytical Methods. Product analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector, and the identification of products was confirmed by comparison of retention times and mass spectral fragmentation patterns from authentic samples using a Hewlett-Packard 5972A/5890 Series II GC-MS (EI 70 eV). Both instruments were equipped with a J&W DB-5 5% diphenyl- 95% dimethylpolysiloxane capillary column (30 m x 0.25 mm i.d. with 0.25 μm film thickness). The injector temperature was 280 ºC, and the detector temperature was 305 ºC. The oven was programmed with an initial temperature of 45 ºC, and the temperature was ramped to 300 ºC at 10 ºC/ min and held for 20 minutes. The carrier gas, helium, was set at a constant flow rate of 1.0 mL/min.

Samples were injected four times onto the GC using a HP 7673 autosampler. The products were quantitated, and the data was averaged using the GC-FID output relative to the internal standards. Typical shot to shot reproducibility was ±2% with the exception of the smaller products (<0.1 mol %) in the presence of a large background in which the shot to shot reproducibility was typically ±10%. Response factors were measured with authentic samples or estimated from measured response factors for structurally related compounds and based on carbon number relative to the internal standards (*n*-tetradecane, hexatriacontane, phenanthrene-d_{10} or benz[a]anthracene-d_{12}). The limits of detection (LOD) for the PAHs depended upon the complexity of the sample, but the LOD was typically 1-10 μg/g. Reaction mixtures were also silylated to the trimethysilyl ether with *N,O*-bis(trimethylsilyl)trifluoroacetamide in pyridine (1:2) to determine if the products contained an alcohol functional group.

Results and Discussion

The FVP of plant steroids was investigated to determine if the native sterol skeleton could form PAHs in the absence of bimolecular reactions at a short residence time, and if the steroid structure controls the yield of PAHs produced upon pyrolysis. Previously, stigmasterol and stigmasterol acetate were investigated by FVP over a range of temperatures between 500 - 700 ºC and the products were analyzed by GC and GC/MS. (Stigmasterol acetate was examined because, in plants, sterols are predominantly esterified with long chain fatty acids (C_{12} –C_{24}).[6] The esterfied form can readily undergo 1,2-elimination at moderate temperatures (300 – 550 ºC) to form an olefin and carboxylic acid.[15] Therefore, the pyrolysis of stigmasterol acetate was investigated to determine the product distribution from the pyrolysis of the resulting stigmasta-3,5,22-triene). The resulting data is shown in **Table 1** and it represents an average from two or three FVP runs (product yields typically ±15 %).[7] The possible mechanistic origins of these products has been previously discussed.[7]

The resulting data shows that the FVP of stigmasterol and stigmasterol acetate, the complexity of the pyrolysis product mixtures increases as the temperature increases, with the largest change in the product yield between 600 and 650 ºC for stigmasterol, and between 600 and 700 ºC for stigmasterol acetate (**Table 1**). Both stigmasterol and stigmasterol acetate produce small hydrocarbons, such as propene, butene/butadiene, pentene, and pentadiene, as well as small PAHs, such as benzene, naphthalene, phenanthrene and their alkylated derivatives. However, large 4-ringed PAHs such as chrysene, benz[a]anthracene, and pyrene were also observed. At temperatures below 650 ºC, the major products formed from the FVP of stigmasterol were from the cleavage of the aliphatic chain connected to the steroid D-ring. Similar products were found for stigmasterol acetate in addition to stigmasta-3,5,22-triene. However, only small amounts of PAHs were formed at 600 ºC for both steroids, see **Table 1**. Above 650 ºC, the steroids produce a significant amount of aromatics and alkylated aromatics at the expense of the primary products, as well as numerous minor products, but this investigation focused on the quantitation of the PAHs.

At 700 ºC, conversion of the stigmasterol and stigmasterol acetate was complete and the yields of PAHs were maximized (**Table 1**). The yield of the 3-4 ringed PAHs, including acenaphthylene, phenanthrene, anthracene, pyrene, chrysene, benz[a]anthracene, and their monomethylated derivatives (see **Figure 2** for diagram of limited structures), are ca. 40% greater for stigmasterol acetate than for stigmasterol (**Figure 3**). This suggests that the additional double bond formed from the 1, 2-elimination enhanced PAH formation. Thus, increasing the conjugation in the steroid ring may enhance the unimolecular free radical dehydrogenation reactions to form PAHs. The rate of 1, 2-elimination for stigmasterol acetate was found to be k = 3.1 s1. However, this is ca. 1.8 times faster than the value reported in the literature for cholesterol acetate (k = 1.7 s^{-1}).[16] Thus, the FVP of cholesterol acetate using our experimental conditions, was investigated and is discussed below, to determine its rate constant.

The FVP of β-sitosterol, an important steroid found in woody biomass,[6] was also investigated. Stigmasterol and β-sitosterol are structurally similar, with the exception that the C22-C23 double bond

is hydrogenated in β-sitosterol, see **Figure 1**. The product distribution from the FVP of β-sitosterol was similar to that found in the FVP of stigmasterol except ca. 1.5 times more phenanthrene, methylphenanthrene, and chrysene were produced, and the yield of indene was ca. 8-fold lower (**Tables 1 and 2**).[7] The products from the FVP of stigmasta-3,5-diene at 700 ºC were similar to that found for β-sitosterol, the yield of PAHs, however, increased ca. 15% compared to the β-sitosterol (**Figure 3**). This emphasizes that the additional double bond, which is formed in the A-ring from the dehydration of the stigmasta-3,5-diene, enhances the formation of PAHs in the pyrolysis of steroids under these reaction conditions.

From this previous investigation described above, it was evident that the yields of PAHs were influenced by the steroid structure. Therefore, to further investigate the impact of structural subtleties on the production of PAHs, the FVP of different steroids found in biomass was investigated, including cholesterol, cholesteryl acetate, and dihydrocholesterol, and the yields of the 3-4 ringed PAH products such as acenaphthylene, phenanthrene, anthracene, pyrene, chrysene, benz[a]anthracene, and their monomethylated derivatives were compared. These steroids are similar in structure with the exception of pre-existing double bonds in the B-ring, or the ability to produce double bonds in the A-ring. That is, in stigmasterol, β-sitosterol, and cholesterol, the B-ring contains a double bond at the C5 position. Cholesteryl acetate can produce a double bond in the A-ring through 1,2-elimination (as discussed above with stigmasterol acetate). Also, cholesterol, cholesteryl acetate, and β-sitosterol do not have a double bond in the exocyclic alkyl chain. Dihydrocholesterol, which contains no double bonds, was investigated to determine the role of the double bond in promoting PAH formation.

The product yields from the 700 °C FVP of these steroids are shown in **Table 2**. Again, as in stigmasterol and stigmasterol acetate, the steroids were found to produce small hydrocarbons, such as propene, butene/butadiene, pentene, and pentadiene as well as small aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, etc., but the product distribution was dependent on the steroid structure. The yield of acenaphthylene, phenanthrene, anthracene, chrysene, pyrene, benz[a]anthracene, and their monomethylated derivatives, were similar for stigmasterol, cholesterol, and β-sitosterol, but these yields were 3.9-5.7 times higher than that found for dihydrocholesterol (see **Figure 3**). Dihydrocholesterol (which contains no double bond in the B-ring) produced very few PAHs at 700 °C and is clearly the least reactive steroid in the set. Thus, it is apparent that having a pre-existing double bond in the B-ring allows for the production of more PAHs by enhancing dehydrogenation reactions.

As suggested by the previous investigation of stigmasterol acetate, esterified sterols could have different reaction pathways, compared to the free sterol, due to their ability to undergo 1,2-elimination at moderate temperatures to form an olefin and carboxylic acid.[15] Therefore, the pyrolysis of cholesteryl acetate was investigated at 500 ºC, to determine the conversion of major products, and 700 ºC to determine the PAH yields.

The major pyrolysis product at 500 ºC was cholesta-3,5-diene, which occurs from the 1,2-elimination of the acetic acid, with a rate constant of $k = 3.2\ s^{-1}$. This is similar to the rate constant of stigmasterol acetate, and confirms that our experimental technique is reproducible. At 700 ºC, the products are similar to that found from stigmasterol acetate. However, in comparison to cholesterol, the yields of the PAHs were enhanced for the cholesteryl acetate ca. 21% where phenanthrene, anthracene and their methylated derivatives contribute the greatest to the increase. This suggests, as before with stigmasterol acetate, that the formation of the additional double bond from the elimination of acetic acid in the A-ring, enhances the unimolecular free radical dehydrogenation reactions to form PAHs.

Removing the double bond from the exocyclic alkyl chain, as in cholesterol and β-sitosterol, did not have a significant effect on the products produced, however the yield of PAHs, increased ca. 20% as compared to stigmasterol. Thus, the largest effect on PAH production lies within the B-ring of the steroid as shown by removing the double bond in the dihydrocholesterol, where PAH production is significantly reduced. The ability to produce a double bond in the A-ring through dehydration, has the effect of increasing the production of PAHs as shown with the esterified sterols.

Overall, it is surprising to find a linear PAH like anthracene, and larger PAHs, such as chrysene, and benz[a]anthracne, which indicates that the steroid skeleton had rearranged. However, no five ringed PAHs such as benzo[a]pyrene were detected (detection limit of 0.005 mg/g) from the FVP of the steroids at 700 ºC. But, most importantly, this concludes the hypothesis that these steroid structures can form PAHs in the absence of bimolecular reactions.[17,18]

Conclusions

Collectively, the results show that PAHs, such as phenanthrene, can be formed at 700 ºC by a series of unimolecular reactions, and the yield of PAHs depends on the steroid structure. The yield of PAHs was influenced by the number and placement of double bonds in the steroid. When a double bond was removed from the steroid B-ring (i.e., dihydrocholesterol), the PAH formation decreased significantly (ca. a factor of 4). Double bonds in the A-ring formed from 1,2-eliminations reactions increased PAH formation. Thus, PAH production was influenced by the efficiency of the elimination. If a double bond was removed from the alkyl chain (for example, comparing stigmasterol to β–sitosterol), there was only a small increase in PAH formation. Overall, this indicates that internal double bonds promote dehydrogentation reactions that lead to enhanced PAH production through unimolecular reactions.

The next question that arises from the investigation is, what effect does the addition of a double bond in the B-ring have? To explore this idea, we plan to investigate the FVP of ergosterol at 700 °C, which contains two double bonds in the B-ring. To provide additional evidence to the structural origins of the products, the FVP of ^{13}C labeled cholesterol (4-^{13}C, 99%) will also be performed and the products of the cholesterol and ^{13}C cholesterol will be compared using the mass spectrum from the GC/MS. These results and the conclusions drawn from their experiments will be discussed at the presentation and in future publications.

Acknowledgment

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC, and supported by Philip Morris USA. MKK was supported by an appointment to ORNL

Postdoctoral Research Associated program administered jointly by Oak Ridge Institute for Science and Education and ORNL.

References

1. (a) Elliot, D. C. In *Pyrolysis Oils From Biomass*; Doltes, E. J.; Milne, T. A.; Ed.; ACS Symposium Series 376; Washington, D. C., 1988; pp. 55-65. (b) *Fundamentals of Thermochemical Biomass Conversion*; Overend, R. P.; Milne, T. A.; Mudge, L. K., Ed.; Elsevier Allplied Science: London, 1985.
2. Homann, K. H. *Angew. Chem. Int. Ed.*, **1998**, *37*, 2434.
3. Bridgwater, A. V.; Boocock, D. B. B.; *Developments in Thermochemical Biomass Conversion*; Blackie Academic: London, 1997.
4. Elliott, D. C.; Beckman, D.; Bridgwater, A. V.; Diebold, J. P.; Gevert, S. B.; Solantausta, Y. *Energy Fuels* **1991**, *5*, 399.
5. Zinkel, D. F. In *Organic Chemicals from Biomass*; Goldstein, I. S, Ed.; CRC Press: Boca Raton, Fl, 1981; pp. 163-187.
6. Barton G. N. In *Organic Chemicals from Biomass*; Goldstein, I. S., Ed.; CRC Press: Boca Raton, Fl, 1981, pp. 249-280.
7. Britt, P. F.; Buchanan, III, A. C.; Kidder, M. K.; Owens, C.; Ammann, J. R.; Skeen, T. J.; Luo, L.; paper submitted to *Fuel*, **2000**.
8. Britt, P. F.; Buchanan, III, A. C.; Cooney, M. J.; Martineau, D. R. *J. Org. Chem*., **2000**, *65*, 1376.
9. (a) Gassiot-Matas, M.; Julia-Danes, E.; *Chromatographia*, **1976**, *9*, 151. (b) Gassiot-Matas, M.; Julia-Danes, E.; *Chromatographia*, **1972**, *5*, 493.
10. Menger, F. M.; Hopkins, J. J.; Cox, G. S.; Maloney, M. J.; Bayer, F. L. *Anal. Chem*., **1978**; *50*, 1135.
11. Trahanovsky, W. S.; Ong, C. C.; Paraky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem*., **1971**, *36*, 3575.
12. Trahanovsky, W. S.; Ong, C. C.; Lawson, J. A. *J. Am. Chem. Soc*., **1968**, *90*, 2839.
13. (a) Taylor, R.; Smith, G. G.; Wetzel, W. H. *J. Am. Chem. Soc*., **1962**, *84*, 4817. (b) Norfolk, S. B.; Taylor, R *J. Chem. Soc, Perkin Trans. II*. **1972**, 280.
14. (a) Seybold, G. *Angew. Chem. Int. Ed. Engl*. **1977**, *16*, 365. (b) Golden, D. M.; Spokes, G. N.; Benson, S. W.; *Angew. Chem. Int. Ed*., **1973**, *12*, 534.
15. DePuy, C. H.; King, R. W. *Chem. Rev*. **1960**, *60*, 431.
16. O'Connor, G. L.; Nace, H. R. *J. Am. Chem. Soc*., **1953**, *75*, 2118.
17. Badger, G. M.; Donnelly, J. K.; Spotswood, T. M.; *Aust. J. Chem*., **1965** *18*, 1249.
18. Severson, R. F.; Schlotzhauer, W. S.; Chortyk, O. T.; Arrendale, R. D.; Snook, M. W. *In Polynulear Aromatic Hydrocarbons*, Jones, P.W.; Leber, P.; Ed,; Ann Arbor Science: Ann Arbor, MI, 1979, pp. 217.

Table 1. Product Yields from the FVP of Stigmasterol and Stigmasterol Acetate as a Function of Temperature

	Stigmasterol				Stigmasterol Acetate		
Temperature (°C)	**550**	**600**	**650**	**700**	**500**	**600**	**700**
% Conversion (SM)	25.0	61.2	98.3	100.0	74.8	99.8	100.0
% Conversion (Product)	7.6	22.7	27.9	28.0	78.8	46.0	24.8
% Mass Balance	83.0	61.5	30.6	28.0	104.0	46.2	24.8
Products (mg/g)							
Benzene	0.27	1.18	10.94	18.13	0.00	0.83	7.96
Toluene	0.21	1.74	12.31	17.93	0.25	1.62	17.22
Ethylbenzene	0.00	0.51	3.37	4.51	0.00	0.00	0.00
m,p-Xylene	0.00	0.16	0.63	0.77	0.00	0.10	2.97
Styrene	0.06	0.66	4.97	8.44	0.00	1.22	12.84
o,p-Ethyltoluene	0.00	0.37	2.52	3.39	0.00	0.48	3.19
α,β-Methylstyrene	0.00	0.60	1.34	1.97	0.00	0.34	2.81
o,p-Methylstyrene	0.04	0.27	3.48	4.82	0.01	1.30	5.95
Indan	0.02	0.31	1.82	2.17	0.00	0.25	1.61
Indene	0.00	0.46	5.15	10.54	0.00	0.48	12.75
Methylindene & isomers	0.00	0.78	4.58	7.18	0.00	0.63	9.98
1,2 Dihydronaphthalene	0.00	2.29	2.08	4.44	0.00	0.65	10.71
Naphthalene	0.00	0.19	2.00	4.57	0.00	0.37	9.15
2-Methylnaphthalene	0.00	0.09	0.75	1.61	0.00	0.12	2.59
1-Methylnaphthalene	0.00	0.61	6.48	10.42	0.00	0.87	15.78
1-Ethylnaphthalene	0.00	0.09	1.56	2.56	0.00	0.19	6.06
Acenaphthylene	0.00	0.07	0.58	1.22	0.00	0.11	2.51
Acenaphthene	0.00	0.13	0.48	0.90	0.00	0.08	1.20
Fluorene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenanthrene	0.00	0.13	0.48	0.79	0.00	0.10	1.87
Anthracene	0.00	0.00	0.14	0.30	0.00	0.05	0.60
Methylphen/anth[a]	0.00	0.71	1.77	2.14	0.00	0.00	3.27
Fluoranthene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyrene	0.00	0.00	0.00	0.31	0.00	0.00	0.55
Methylpyrenes	0.00	0.00	0.00	1.14	0.00	0.00	0.36
Benz[a]anthracene	0.00	0.00	0.16	0.11	0.00	0.00	0.28
Chrysene	0.00	0.00	0.30	0.16	0.00	0.00	0.26
Methylbenz[a]anth/chrys[b]	0.00	0.00	0.26	0.56	0.00	0.00	0.00
3,5,22-Stigmastatriene	81.01	87.36	12.42	5.01	752.29	317.10	0.00

[a]Methylphenanthrene/anthracene. [b]Methylbenz[a]anthracene/chrysene.

Table 2. Product Yields from the FVP of Steroids at 700 ºC

	b-Sito[a]	3,5-Diene[b]	Chol[c]	Chol Acet[d]	Dihydr[e]
% Conversion (SM)	100.00	95.64	94.80	100.00	95.70
% Conversion (Product)	22.56	7.85	26.40	39.20	34.70
% Mass Balance	22.56	7.85	31.70	39.20	39.00
Products (mg/g)					
Benzene	16.94	-[h]	11.17	12.38	9.12
Toluene	18.89	-[h]	23.61	20.05	19.18
Ethylbenzene	5.87	2.66	5.64	6.77	4.59
m,p-Xylene	3.87	1.53	4.05	3.07	3.42
Styrene	9.05	5.73	10.08	16.40	4.12
o,p-Ethyltoluene	3.66	2.41	4.87	4.09	4.32
α,β-Methylstyrene	1.96	1.68	2.10	3.01	1.62
o,p-Methylstyrene	5.10	3.55	5.72	5.53	4.44
Indan	1.39	0.91	1.62	1.19	1.33
Indene	1.37	0.90	8.03	8.76	4.77
Methylindene & isomers	7.80	7.28	9.89	13.58	1.56
1,2 Dihydronaphthalene	4.28	7.05	3.83	7.50	1.66
Naphthalene	5.05	6.81	4.31	7.29	1.75
2-Methylnaphthalene	2.11	2.28	2.04	2.08	1.03
1-Methylnaphthalene	5.00	7.16	5.47	7.45	1.27
1-Ethylnaphthalene	5.68	4.73	3.28	4.88	1.05
Acenaphthylene	2.69	2.06	1.78	2.25	0.80
Acenaphthene	1.37	0.89	0.86	0.99	0.59
Fluorene	0.00	0.00	1.61	1.71	0.19
Phenanthrene	1.20	2.61	1.27	2.05	0.25
Anthracene	0.42	0.87	0.46	0.90	0.20
Methylphen/anth[f]	2.93	2.79	2.34	3.31	0.49
Fluoranthene	0.00	0.00	0.14	0.11	0.00
Pyrene	0.22	0.42	0.22	0.29	0.00
Methylpyrenes	0.40	0.86	1.45	1.04	0.00
Benz[a]anthracene	0.27	0.14	0.00	0.00	0.00
Chrysene	0.26	0.17	0.38	0.17	0.00
Methylbenz[a]anth/chrys[g]	0.00	0.00	0.00	0.00	0.00

[a]β-sitosterol, [b]3, 5-Stigmastadiene , [c]cholesterol, [d]cholesterol acetate, [e]dihydrocholesterol, [f]methylphenanthrene/anthracene.
[g]Methylbenz[a]anthracene/chrysene, [h]The solvent and solvent imupurities obscured these products.

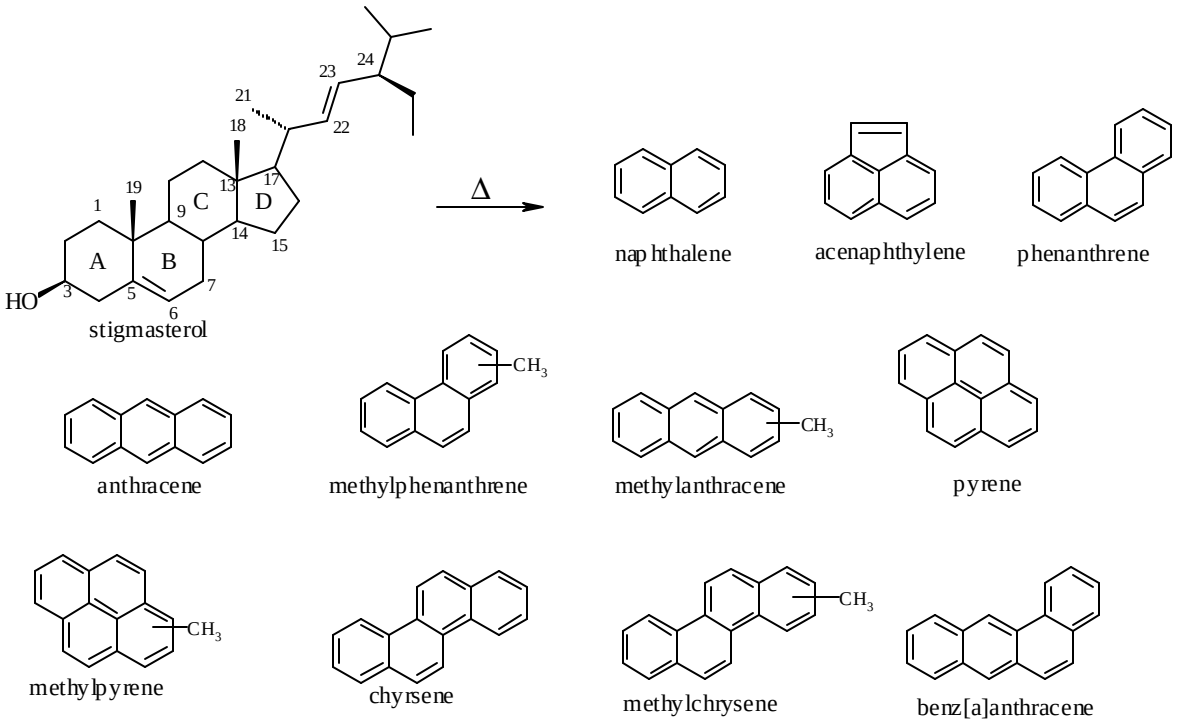


Figure 2. Aromatic products from the FVP of stigmasterol at 700 ºC.

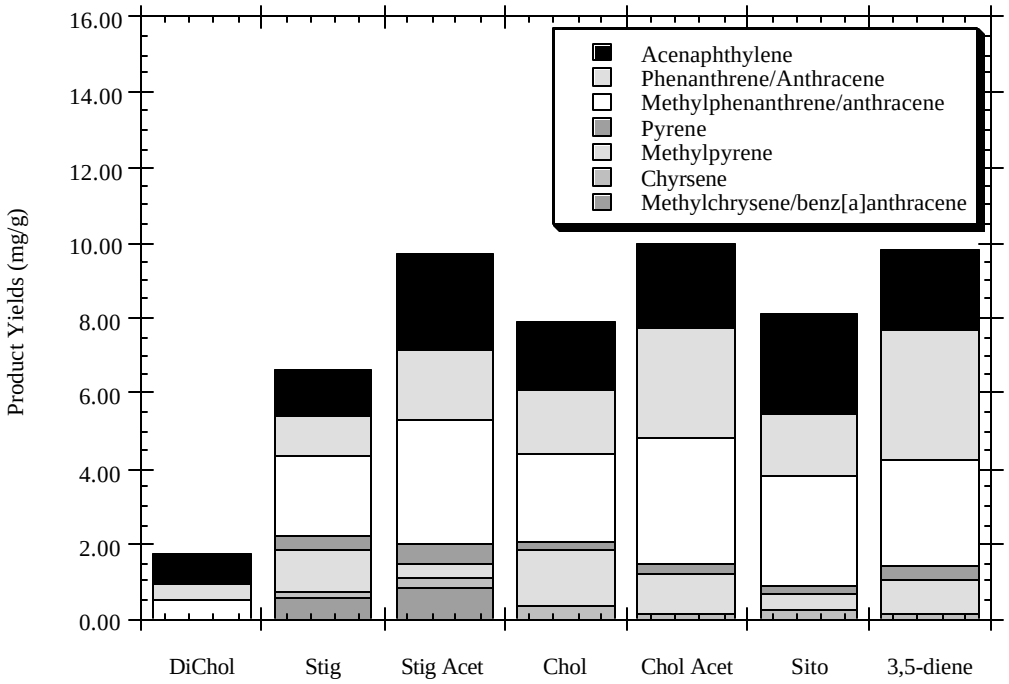


Figure 3. Effect of steroid structure on PAH yields by FVP at 700 ºC. DiChol (dihydrocholesterol), Stig (stigmasterol), Stig Acet (stigmasterol acetate), Chol (cholesterol), Chol Acet (cholesterol acetate), Sito (β−sitosterol), 3, 5-diene (3, 5-stigmastadiene).