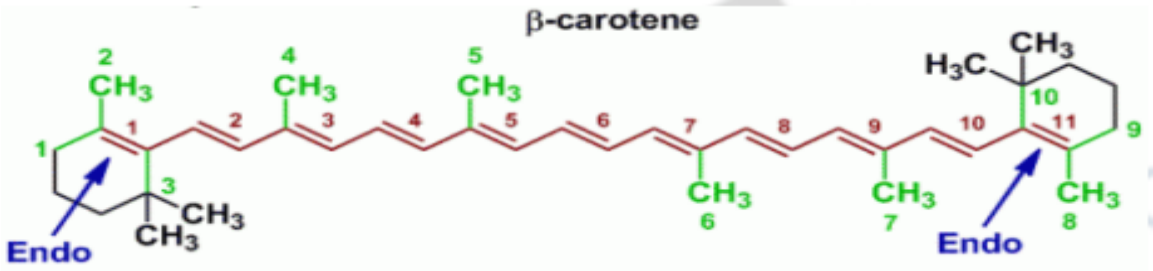
Calculate λ max:

For polyenes with more than 4 conjugated double bonds, Fieser-Kuhn rule is used to calculate λ max Fieser-Kuhn derived the following equation to calculate the wavelength of maximum absorption λ max and also maximum absorptivity ε max

$$\lambda max = 114 + 5x + y\,(48.0 - 1.7\,y) - 16.5\,Rendo - 10\,Rexo$$

- **x (number of alkyl substituents)**
- **y (number of conjugated double bonds)**
- **R endo (number of endocyclic double bonds)**
- **R exo (number of exocyclic double bonds)**



- x (number of alkyl substituents) = 10
- y (number of conjugated double bonds) = 11
- Rendo (number of endocyclic double bonds) = 2
- Rexo (number of exocyclic double bonds) = 0

λmax = 114 + 5x + y (48.0 – 1.7 y) – 16.5 Rendo – 10 Rexo = 114 + 5(10) + 11 (48.0 – 1.7(11)) – 16.5 (2) – 10 (0) = 114 + 50 + 11 (29.3) – 33 – 0 = 114 + 50 + 322.3 – 33 = 453.30 nm

Calculation of λmax of Organic Compounds Using Woodward Fieser Rules

In 1945 Robert Burns Woodward gave certain rules for correlating λmax with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental

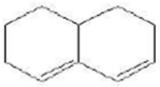
data, and the modified rule is known as Woodward-Fieser Rules. It is used to calculate the position and λmax for a given structure by relating the position and degree of substitution of chromophore.

WOODWARD- FIESER RULES:

Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

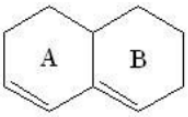
I) CONJUGATED DIENE CORRELATIONS:

Homoannular Diene:- Cyclic diene having conjugated double bonds in same ring.



Heteroannular Diene:- Cyclic diene having conjugated double bonds in different rings.

Endocyclic double bond:- Double bond present in a ring.



Exocyclic double bond: - Double bond in which one of the doubly bonded atoms is a part of a ring

Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

Parent values and increments for different substituents / groups:

I) CONJUGATED DIENE CORRELATIONS:

i) Base value for an unsubstituted, conjugated, homoannular diene = 253 nm

ii) Base value for an unsubstituted, conjugated, acyclic or heteroannular diene = 214 nm

Increments for:

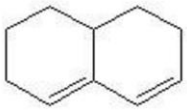
Each extra double bonds in conjugation	+ 30 nm
Exocyclic double bond (effect is twofold if the bond is exocyclic to two rings)	+ 5 nm

Substituent effect:

A. -OCOR or –OCOAr	+ 0 nm
B. Simple alkyl substituents or ring residue	+ 5 nm
C. Halogen (-Cl, -Br)	+ 5 nm
D. OR (R=Alkyl)	+ 6 nm
E. SR (R=Alkyl)	+ 30 nm
F. NR_2 (R=Alkyl)	+ 60 nm

Eg:

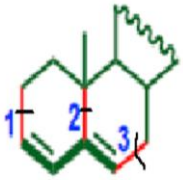
1.



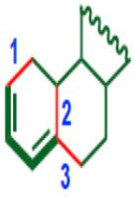
Base value = 214 nm
Ring residue = 3 x 5 = 15 nm

Exocyclic double bond = 1 x 5 = 5 nm

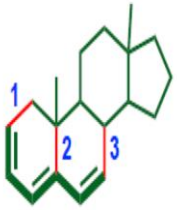
λ_{max} = 214 + 15 + 5 = 234 nm



base value : 214 nm
3 ring residues : +15
1 exocyclic C=C : + 5 .
Total λ_{max} : 234 nm
Observed : 235 nm



base value (Homoannular) : 253 nm
3 ring residues : +15
1 exocyclic C=C : + 5
Total λ_{max} : 273 nm (Observed : 235 nm)



base Value: 253 nm
3 Ring residues: +15
1 Exocyclic C=C: + 5
Double-bond Extending Conjugation: +30 .
Total λ_{max} : 303 nm
Observed: 304 nm

II) ENONE:

Rules of Enon & Dienone Absorption

Base values:

i. Acyclic α,β-unsaturated ketones 215 nm

ii. 6-membered cyclic α,β-unsaturated ketones 215 nm

iii. 5-membered cyclic α,β-unsaturated ketones 202 nm

iv. α,β-unsaturated aldehydes 210 nm

v. α,β-unsaturated carboxylic acid & esters 195 nm

Increments for:

Double bond extending conjugation (DEC): +30

Exocyclic double bond: + 5

Homodiene component: +39

Alkyl group/ring residue: α position +10, β position +12, γ & higher position +18

Polar groups:

-OH: α position +35, β position +30, δ position +50

-OAc: α, β, γ + 6

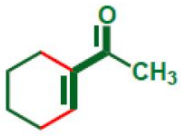
-OMe: α +35, β +30 γ +17 δ +31

-Salk(sample alkaloide): β +85

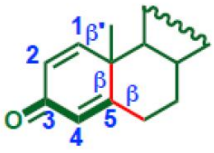
-Cl: α +15 β +12

-Br: α +25 β +30

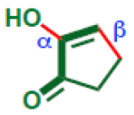
-NR2: β +95



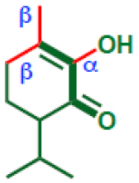
Base value:	215 nm
α substituent:	+10
β substituent:	+12
Total:	237 nm
Observed:	232 nm



$\Delta^{4,5}$ system (base):	215 nm
2 β substituents:	+24
1 exocyclic C=C:	+ 5
Total:	244 nm
Observed:	245 nm



Base value:	202 nm
β substituent:	+12
α-OH:	+35
Total:	249 nm
Observed:	247 nm



Base value:	215 nm
2 β substituents:	+24
α-OH:	+35
Total:	274 nm
Observed:	270 nm