

# GLYCOSIDES – FLAVOR ENHANCERS IN TOBACCO SMOKE

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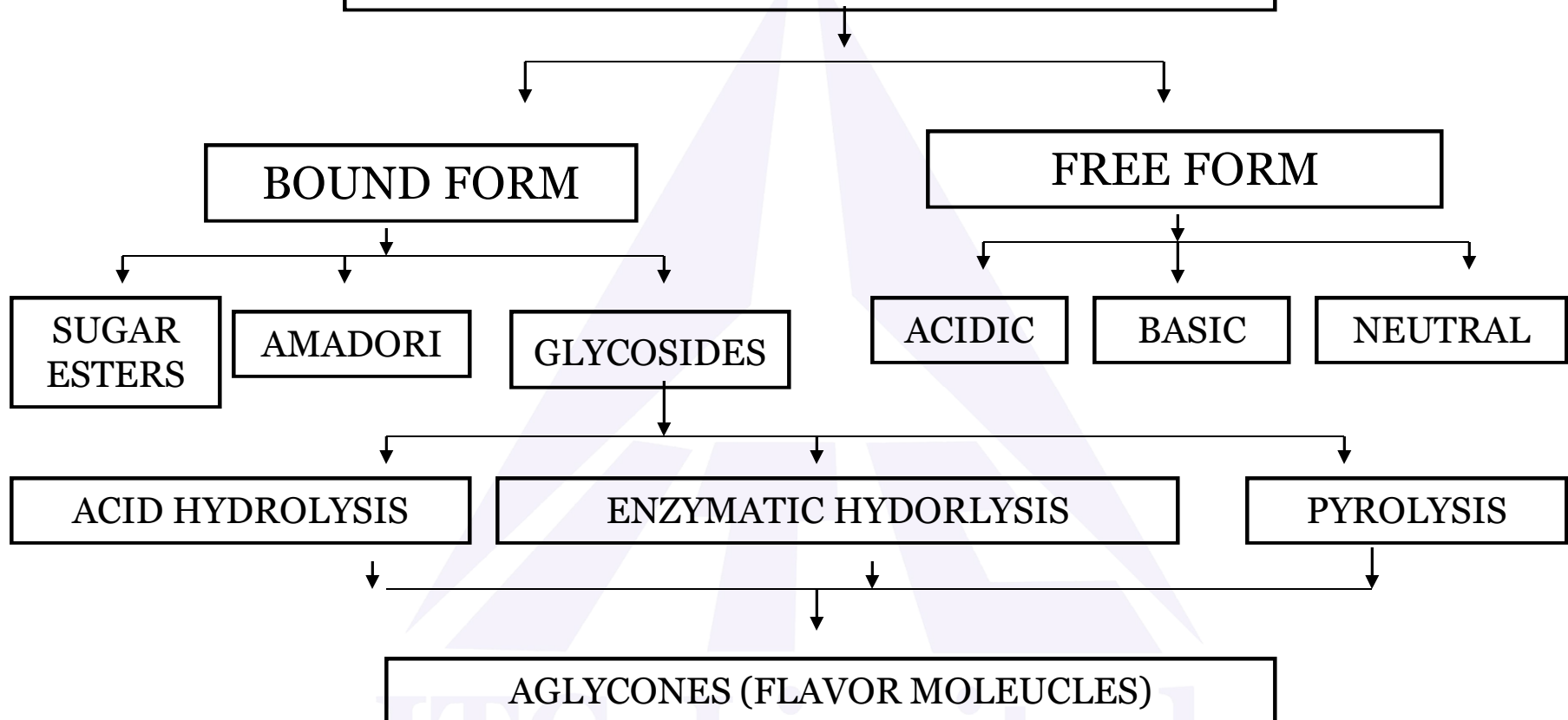
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# TOBACCO FLAVOR

## TOBACCO FLAVOR COMPOUNDS



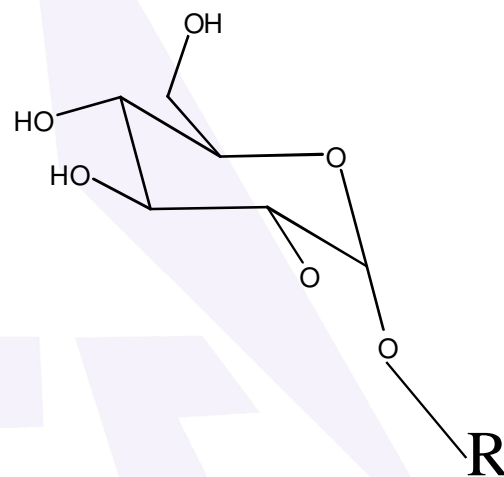
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# OBJECTIVE

- To synthesize Menthol glycoside and evaluating the sensory / flavor enhancement in Cigarette

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# GLYCOSIDE



R = AGLYCONE

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# BACKGROUND

- ❖ Glycosides are non volatile sugar precursors which are bound to aroma compounds which positively enhance the smoke flavor of tobacco on pyrolysis.
- ❖ In the free forms (aglycones) these compounds produce a less specific tobacco smoke sensation.
- ❖ Bound form positively influences smoke characteristics such as “ Sweet aromatic” and “typically tobacco like”
- ❖ During smoking aglycones (flavor compounds) which are volatile and pass in smoke.

## **Ref :**

- Tobacco Leffingwell reports vol.1, 2001
- Georg. F K., Siegfried nitz and Friedrich Drawert ,Bound aroma compounds in tobacco smoke condensate.Zeitschrift fur lebensmitteluntersuchung 188.vol .6,1986,512-516.
- Stahl –Biskup ,Glycosidically bound volatiles- A review 1986-1991, Vol 8,1993,61-80

# GLYCOSIDES IN TOBACCO

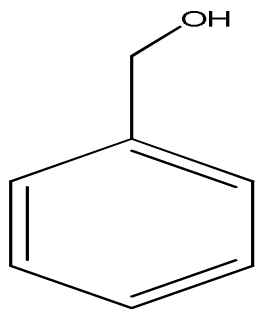
Glycosides in tobacco are

- Norcarotenoids
- Ionone related compounds
- Polyphenols such as Scopoletin, Rutin and Kaempferol

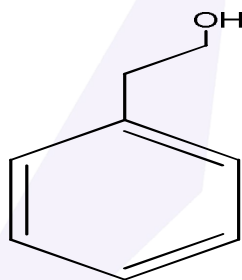
## **Ref:**

- Kafer, georg .F et al., Bound aroma compounds in tobacco smoke condensate , Zeitschrift fur lebensmitteluntersuchung 188.vol .6,1986,512-516.

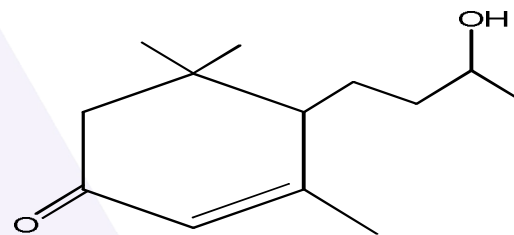
# AGLYCONES PRESENT AS GLYCOSIDES



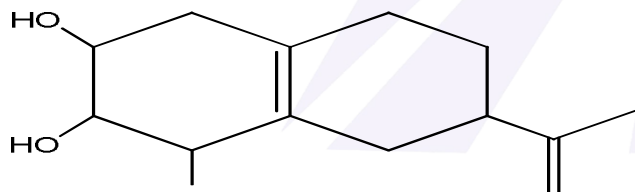
Benzyl alcohol



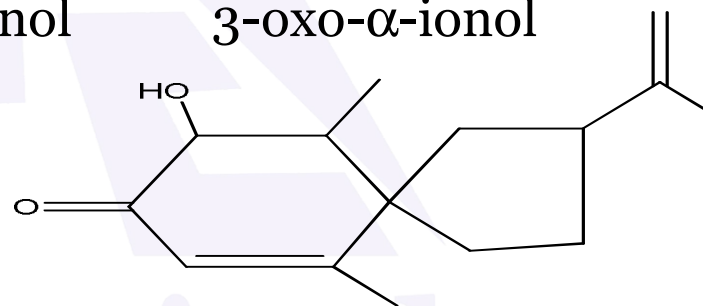
2-Phenylethanol



3-oxo- $\alpha$ -ionol



Rishitin



Spirovetivan A

## Ref:

•Kafer, georg .F et al., Bound aroma compounds in tobacco smoke condensate , Zeitschrift fur lebensmitteluntersuchung 188.vol .6,1986,512-516.



# INCREASE OF AGLYCONES ON ACID HYDROLYSIS

COMPOUND NAME	AMOUNT (mg/100g) pH 7.00	AMOUNT (mg/100g) pH 2.50
N-TETRA DECANE (INTERNAL STANDARD)		
Furfural	0.55	1.08
Phenyl acetaldehyde	0.31	0.43
Furfuryl alcohol	0.20	0.43
Solanone	2.68	3.54
beta-Damascone	0.09	0.19
Damascenone	0.88	1.35
Geranyl acetone	0.36	0.40
Benzyl alcohol	0.52	0.70
Phenylethyl alcohol	0.68	0.89
beta-ionone	0.15	0.31
Neophytadiene	27.18	38.12
Methyl palmitate	0.80	0.92
Megastigmatrienone	9.44	11.53

There is an increase in flavor compounds during acid treatment



# MENTHOL GLYCOSIDES



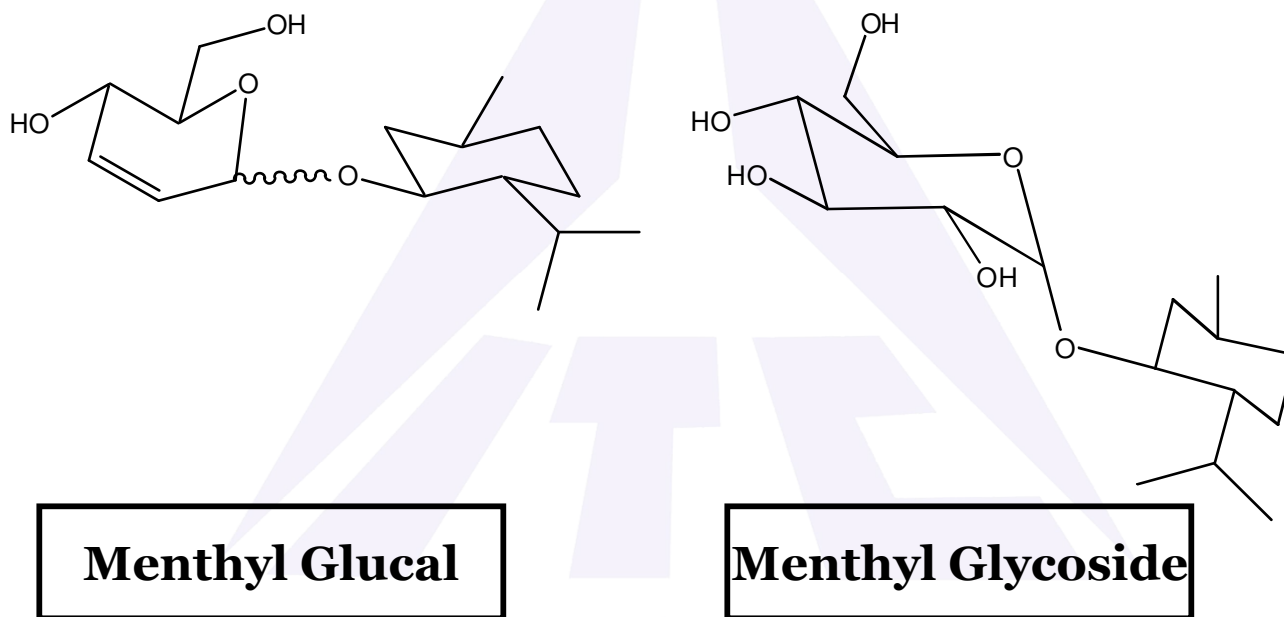
# MENTHOL GLYCOSIDES

- ❖ Menthol because of inherent mint flavor and refreshing feeling have been widely used as additives to medicines, tobacco, liquid creams and pasters for oral introduction etc.
- ❖ Isao sakata et al first reported the Isolation of l-menthyl - $\beta$ - D-glucopyronoside from Japanese pepper mint
- ❖ Menthol is extensively used in tobacco products because of refreshing cooling effect it imparts to tobacco smoke.
- ❖ Unfortunately, the high degree of volatility and ease of sublimation of menthol have presented problems during manufacturing, packaging and handling process .

## Ref :

- Isao sakata,et al in Synthesis and paroperties of menthyl glycosides from Agric. Biol. Chem , 43(2),307-312,1979
- Philip Christenson,et al., Menthyl pyran and smoking composition compounds US Patent No 5137579, 1992

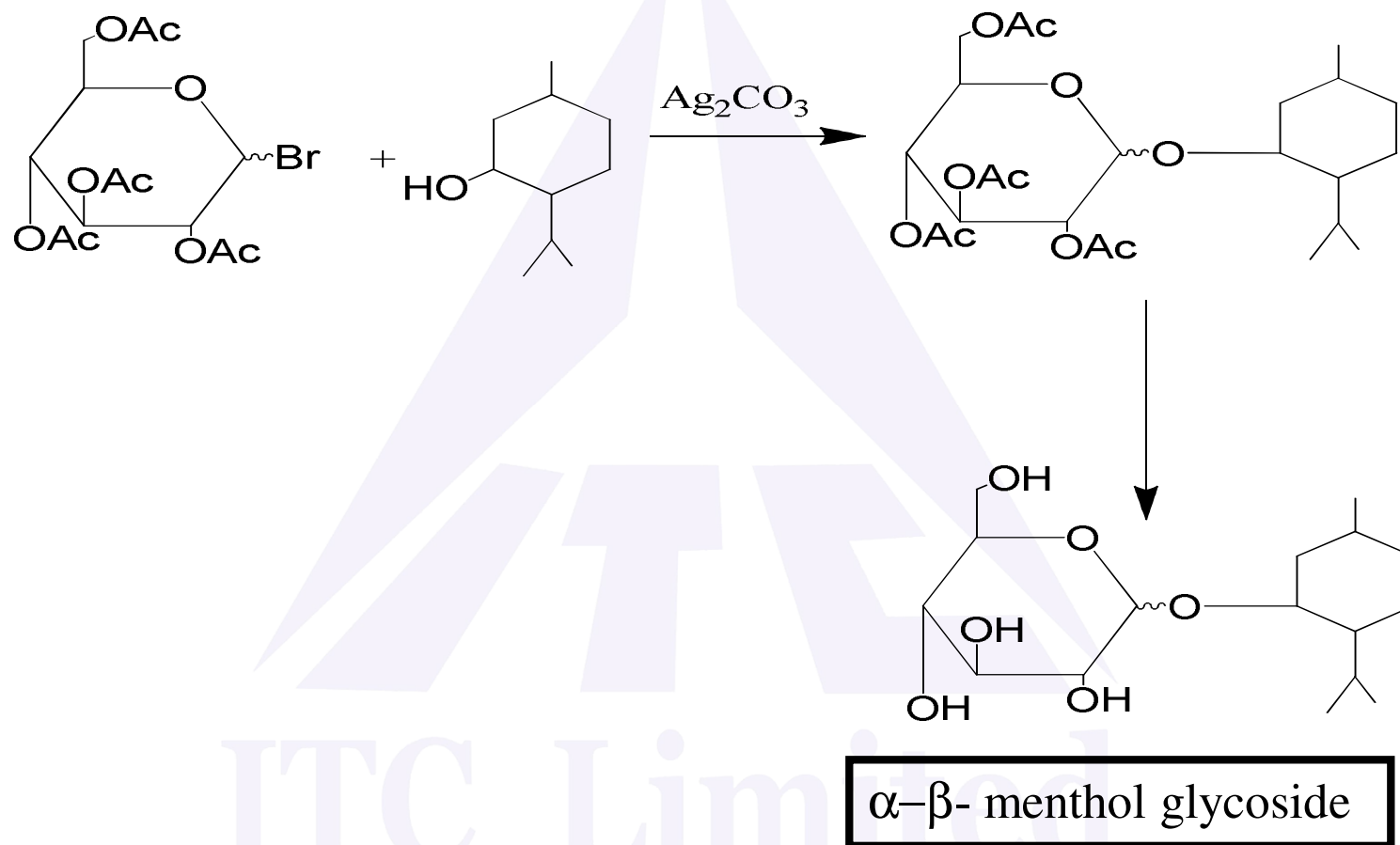
# MENTHOL GLYCOSIDE



**Ref:**

Iwamura et al., Agri.Bio.Chemistry , 43 (2), 307-312 (1979).

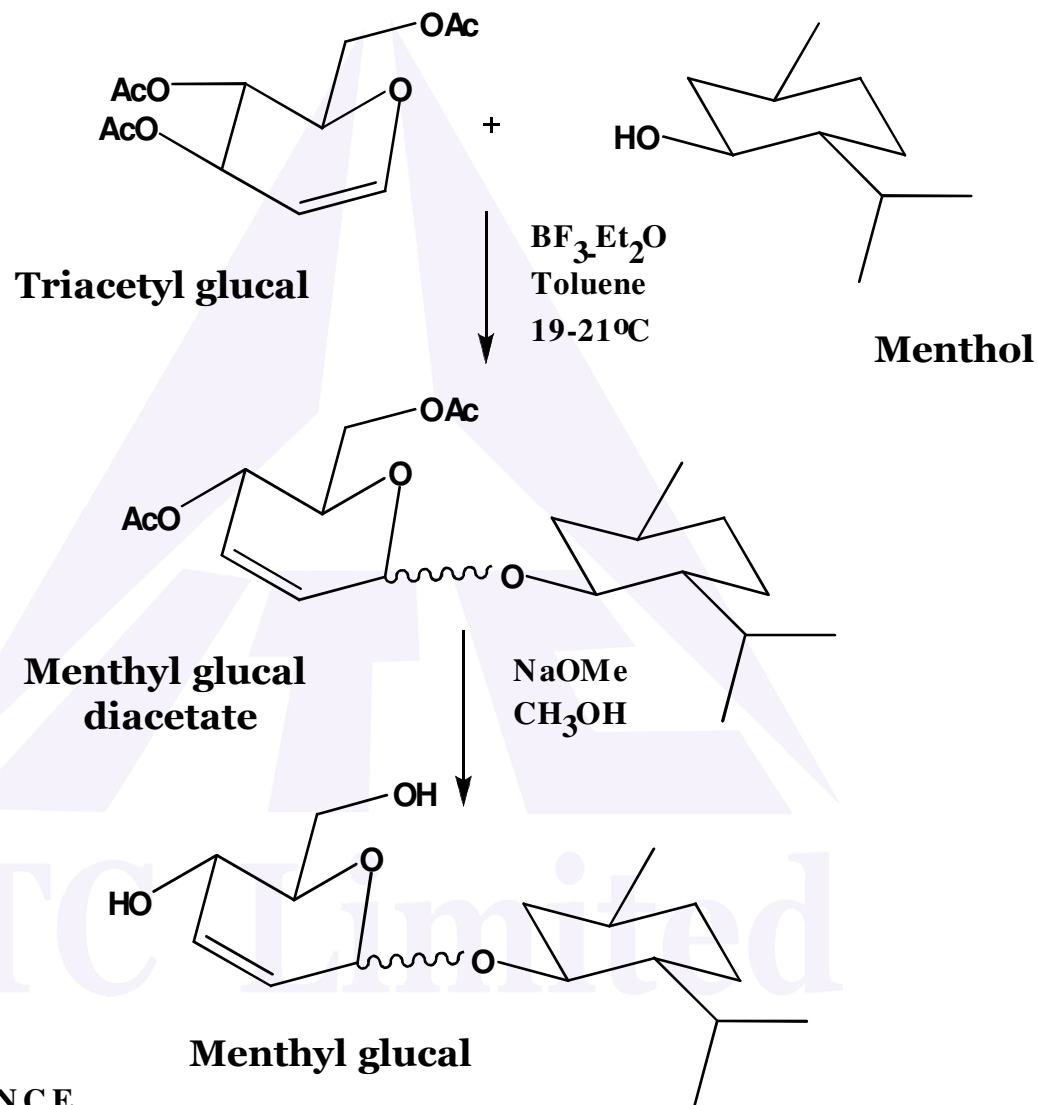
# SYNTHESIS OF MENTHOL GLYCOSIDE



Isao sakata et al., Synthesis and properties of menthyl glycosides , Agric. Biol. Chem, 43(2),307-312,1979

# SYNTHESIS

## LITERATURE BACKGROUND



## REFERENCE

Menthyl pyran and smoking compositions compound  
US Patent No : 5137579 (1992)

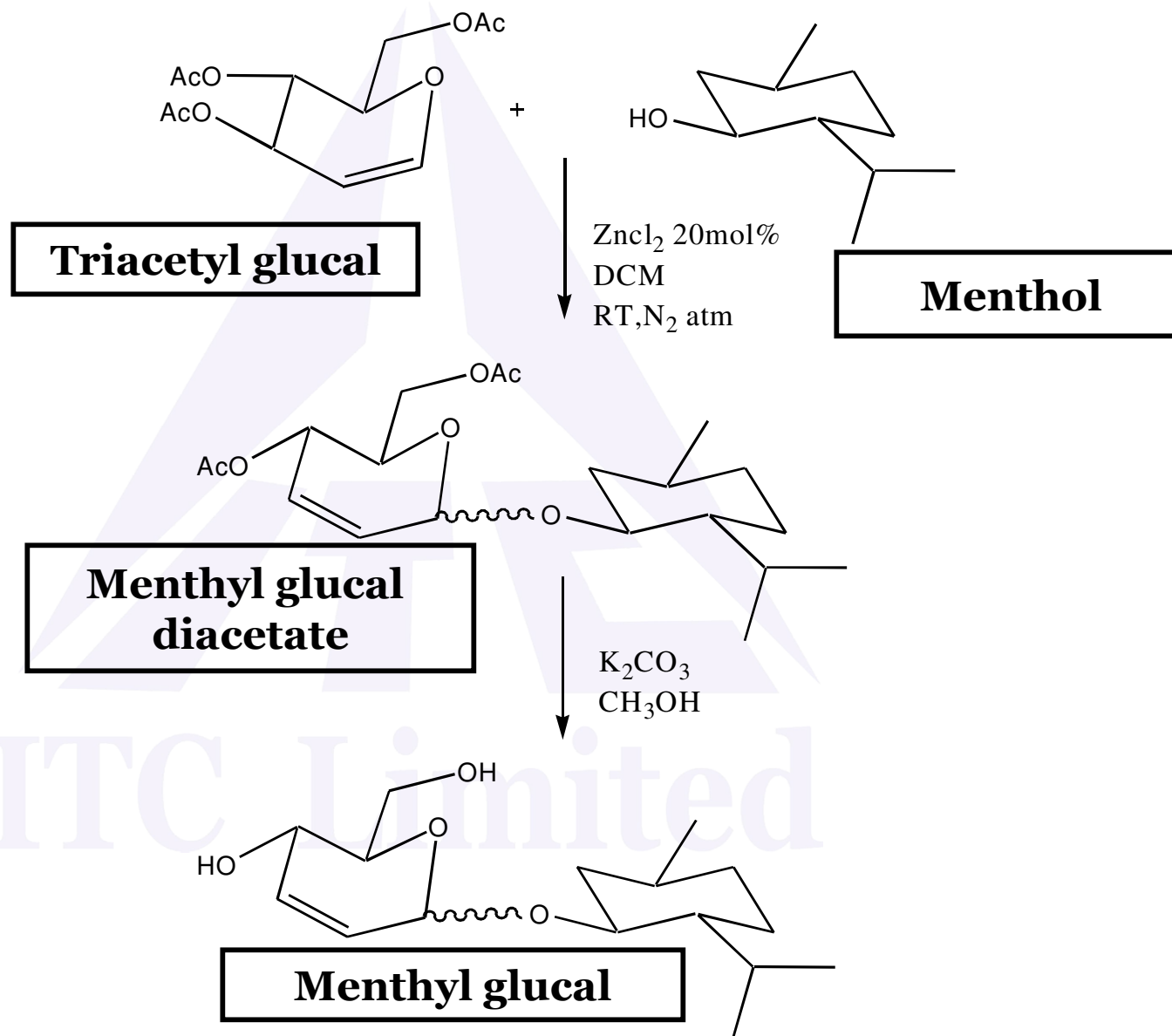
# LIMITATIONS OF LITERATURE METHODS

- ❖ Bromoacetyl glucose is not stable
- ❖ Isolation of the Menthol glycoside
- ❖ Hazardness of the catalyst used
- ❖ Low Yield (around 65%)

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# SYNTHESIS (OUR APPROACH)

## FERRIER REARRANGEMENT





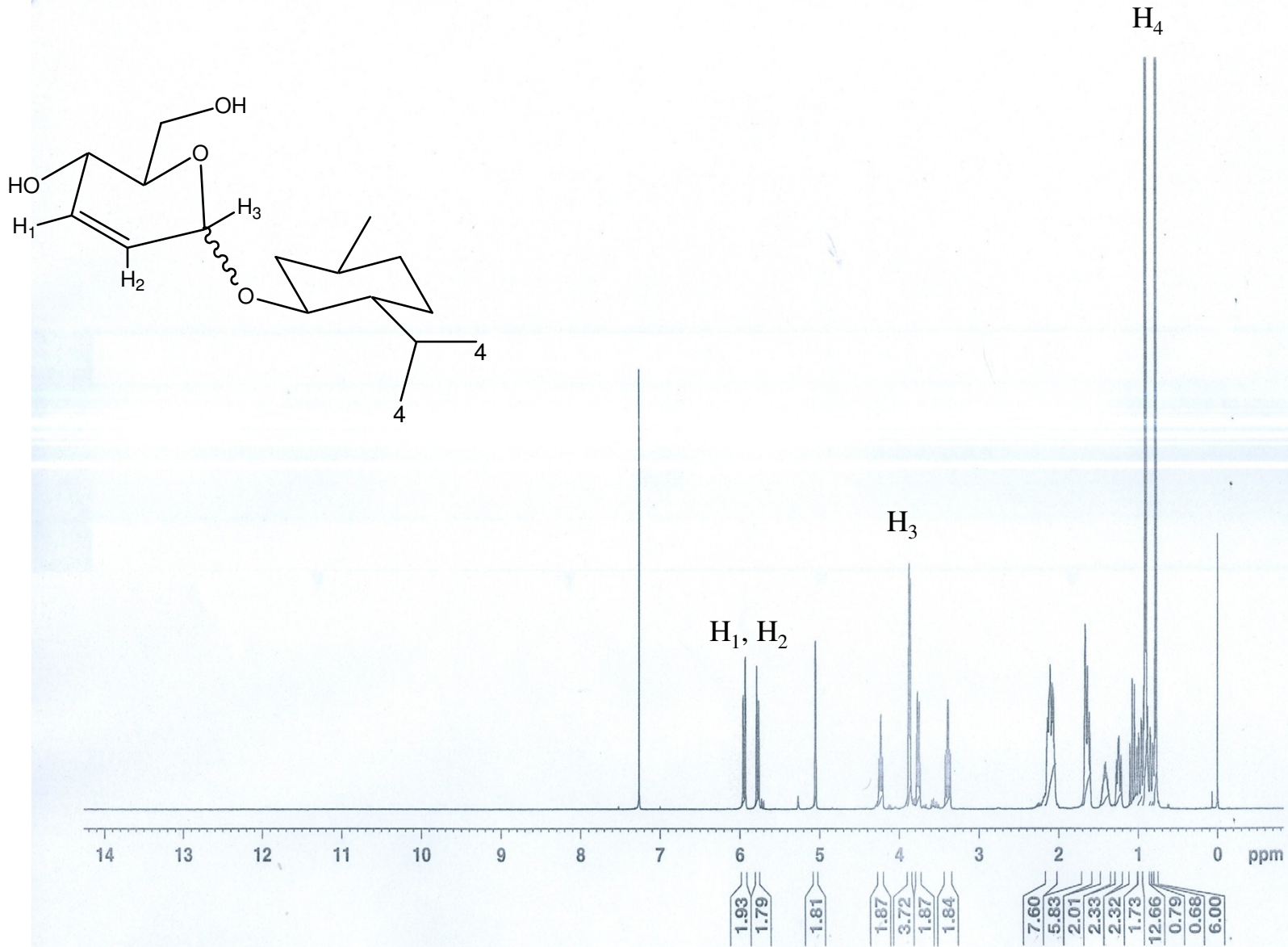
# CHARACTERISATION

✓  $^1\text{H}$  NMR

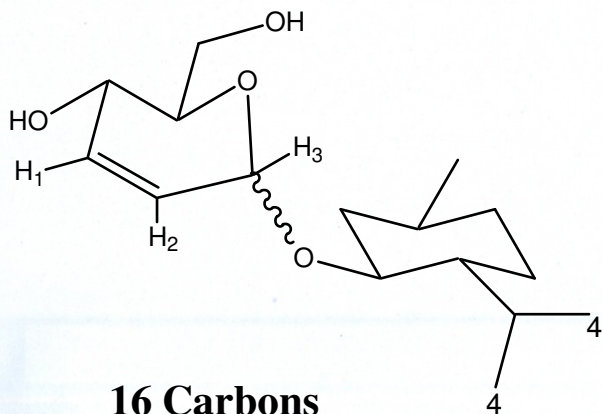
✓  $^{13}\text{C}$



Deve-2



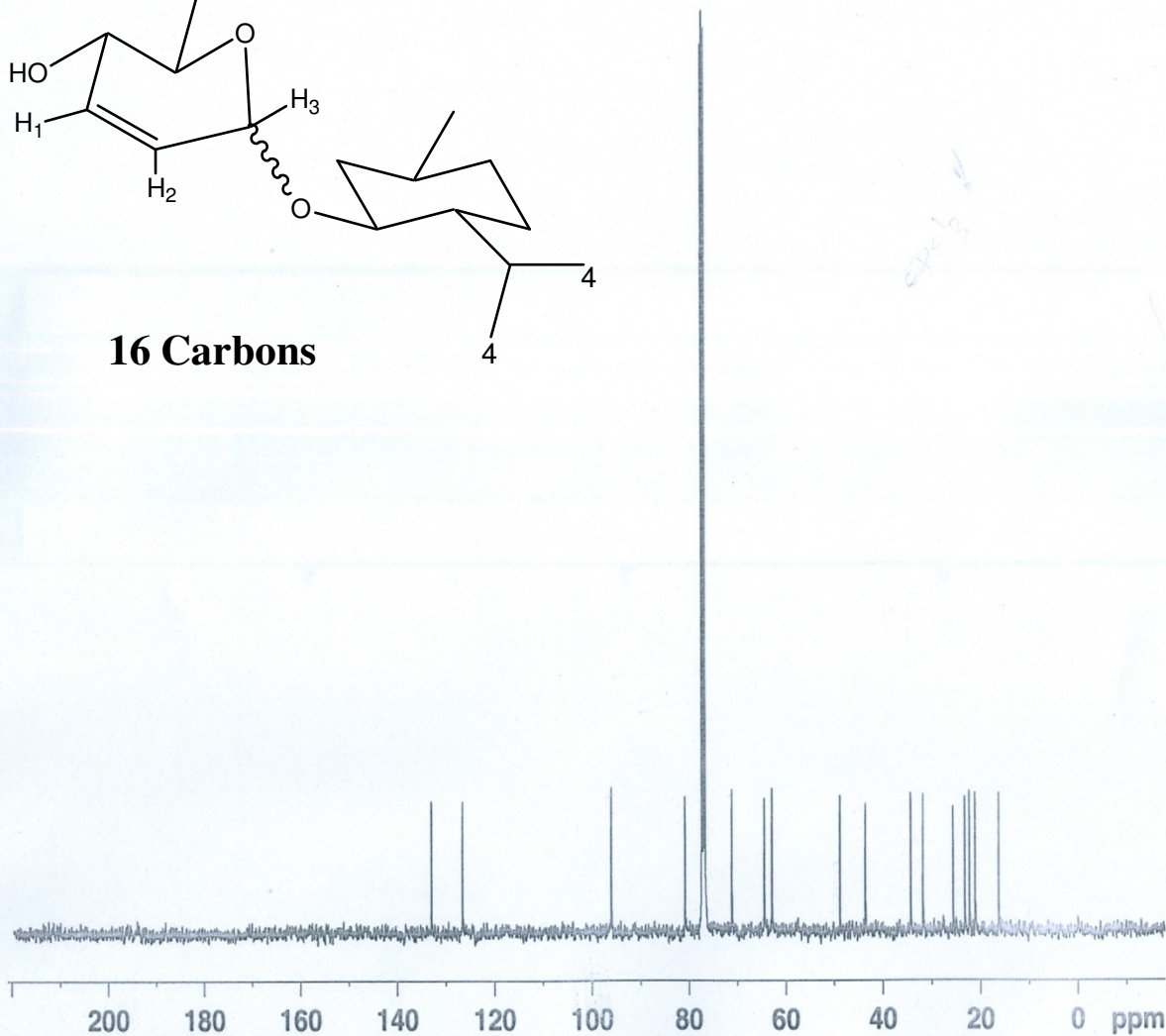
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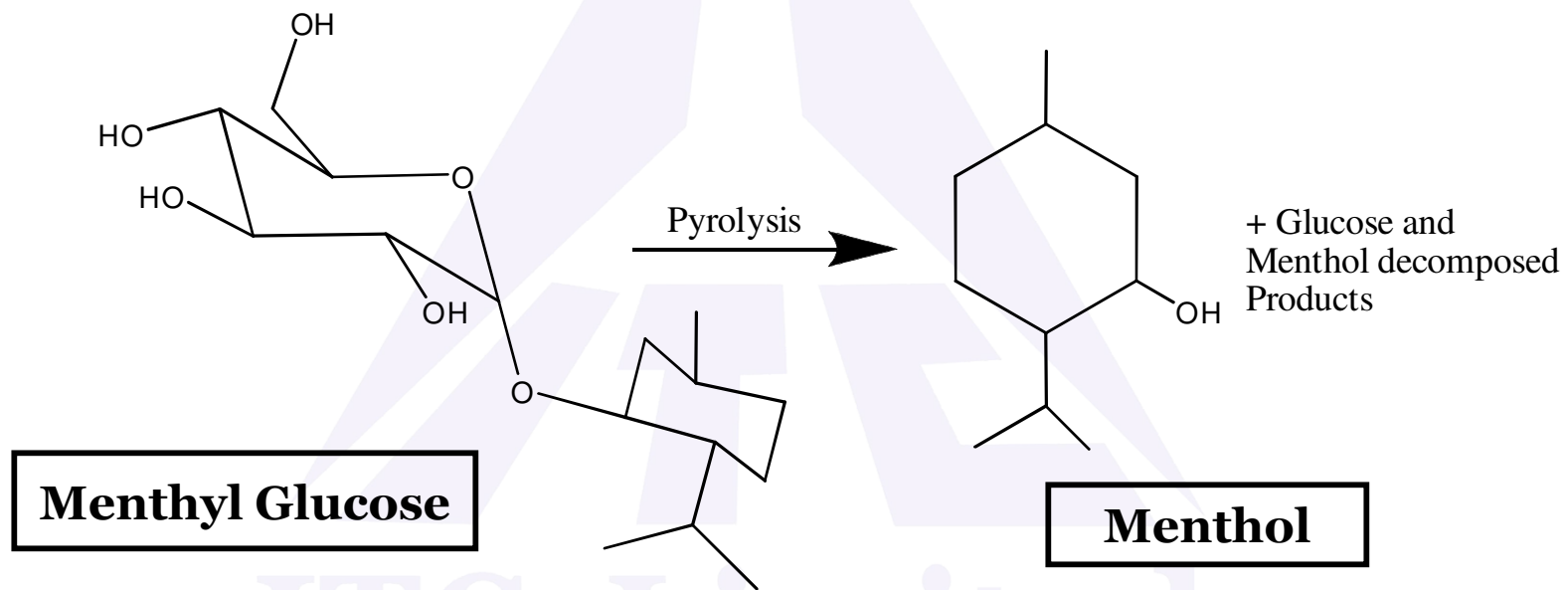
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PL13 12.30 dB  
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PL12W 0.41855475 W  
PL13W 0.39788014 W  
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SI 32768  
SF 100.6379170 MHz  
WDW EM  
SSB 0  
LB 5.00 Hz  
GB 0  
PC 1.40



# THERMAL DECOMPOSITION OF MENTHOL GLYCOSIDE



**Ref:**

Jian Tang et al . Journal of Analytical application pyrolysis 78,180-184 (2007)

# CONFIRMATION OF MENTHOL RELEASE ON PYROLYSIS

- ❖ Glycosides was added in cigarettes and smoked.
- ❖ Volatiles trapped in dichloromethane at  $-70^{\circ}\text{C}$ .
- ❖ GC-MS confirms the presence of menthol in the smoke.
- ❖ No menthol was detected in the Cigarette where there is menthol glycoside.

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# CONCLUSION

- ❖ Positive smoke sensation due to controlled release of the aglycones which is released puff by puff.
- ❖ Menthol glycoside was synthesized in 90% yield using Indium trichloride as a catalyst
- ❖  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR confirms the structure of Menthol glucal.
- ❖ Sensory data confirms cooling effect.

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# ACKNOWLEDGEMENTS

- ITC R&D Centre
- ITD DMC
- Mr.A .Devaraj

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**THANK YOU**

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