Fenil Propanoid

Oleh:

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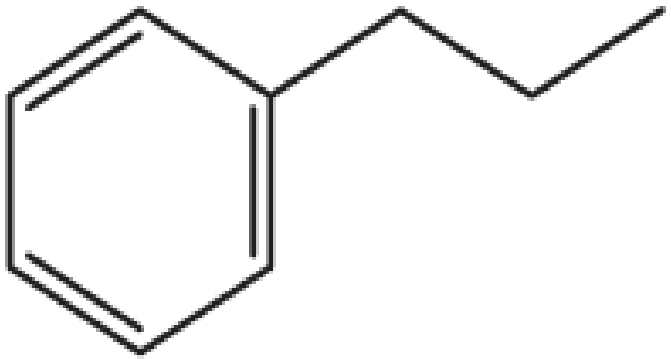
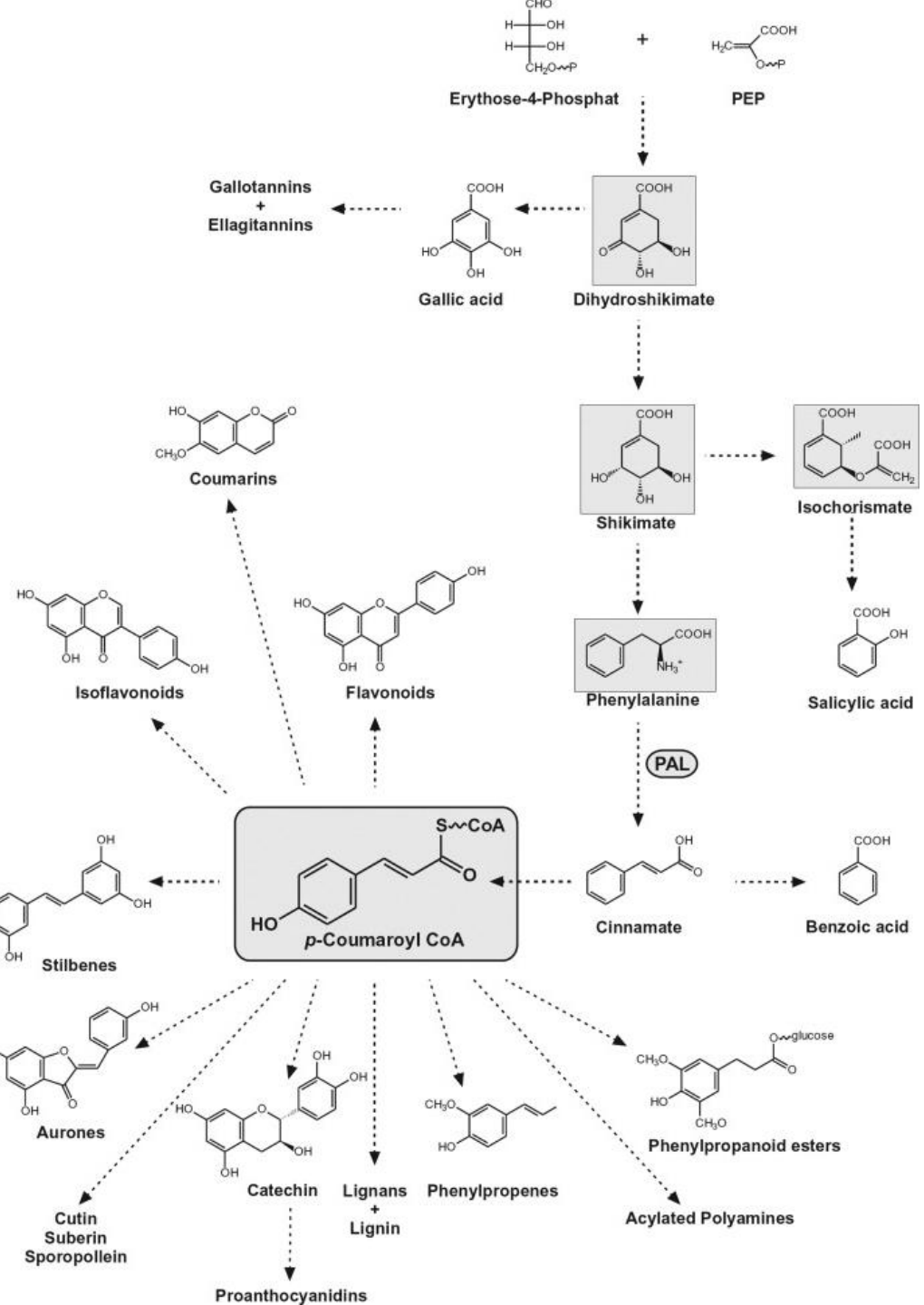
Diah Lia Aulifa, M.Si., Apt

FENIL PROPANOID



Kerangka dasar Fenilpropanoid

Kimia dan Penyebaran	Fenil propanoid → senyawa fenol alam yang mempunyai cincin aromatik dengan rantai samping terdiri atas tiga atom karbon
	Secara biosintesis ,senyawa ini turunan asam amino protein aromatik yaitu fenilalanina dan fenilpropanoid, dapat mengandung satu sisa C6 -C3 atau lebih
	Yang paling tersebar luas → asam hidroksisinamat suatu senyawa yang penting, bukan saja sebagai bangunan dasar lignin tetapi juga berkaitan dengan pengaturan tumbuh dan pertahanan terhadap penyakit.
	Yang termasuk fenilpropanoid: hidroksikumarin, fenilporpena dan lignan.



CIRI UMUM DAN TATA NAMA SENYAWA FENIL PROPANOID

Fenil propanoid merupakan senyawa fenol alam yang mempunyai cincin aromatik dengan rantai samping terdiri dari 3 atom karbon.

Senyawa fenil propanoid yang berasal dari turunan sinamat berwujud kristal putih dan sedikit larut dalam air.

Empat macam asam hidroksi sinamat banyak terdapat dalam tumbuhan: asam ferulat, sinapat, kafeat dan p-kumarat.

Senyawa fenil propanoid merupakan salah satu kelompok senyawa fenol utama yang berasal dari jalur shikimat.

Senyawa-senyawa fenol ini mempunyai kerangka dasar karbon yang terdiri dari cincin benzena (C_6) yang terikat pada ujung rantai karbon propana (C_3).

Tidak ada tata nama yang spesifik untuk senyawa turunan fenil propanoid karena penomorannya tidak selalu dari rantai alifatiknya, yakni propane tetapi dapat juga berdasarkan kerangka karboaromatiknya.

KLASIFIKASI FENIL PROPANOID

1. Turunan sinamat

Asam sinamat memiliki rumus kimia $C_6H_5CHCHCOOH$ atau $C_9H_8O_2$, berwujud kristal putih, sedikit larut dalam air, dan mempunyai titik leleh 133°C serta titik didih 300°C.

Asam sinamat termasuk senyawa fenol yang dihasilkan dari lintasan asam sikimat dan reaksi berikutnya.

Prekursor → fenilalanin dan tirosin sama seperti asam kafeat, asam p-kumarat, dan asam ferulat.

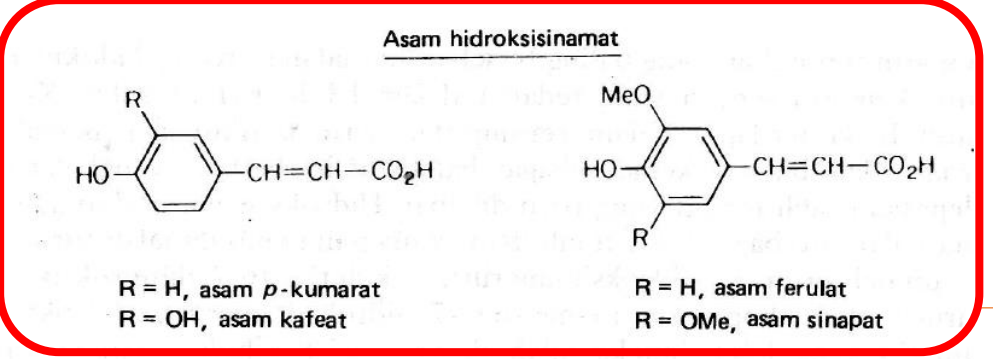
Keempat senyawa tersebut penting bukan karena terdapat melimpah dalam bentuk tak terikat (bebas), melainkan karena mereka diubah menjadi beberapa turunan di samping protein.

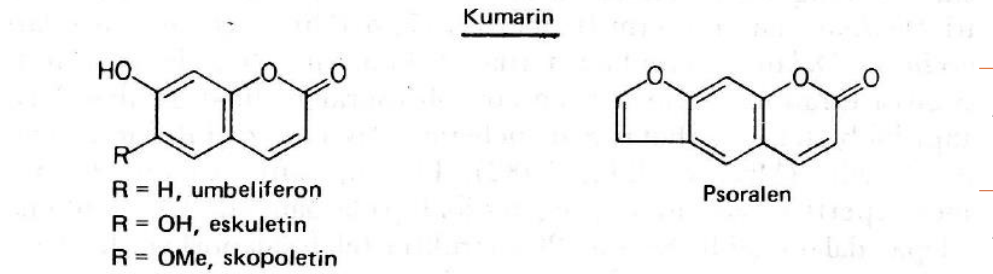
Turunannya termasuk fitoaleksin, kumarin, lignin, dan berbagai flavonoid seperti antosianin.

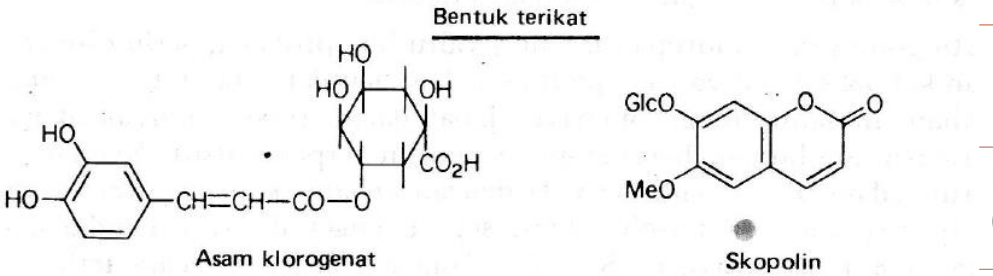
Diklasifikasi sebagai asam karboksilat tak jenuh, ia terjadi secara alami pada sejumlah tanaman.

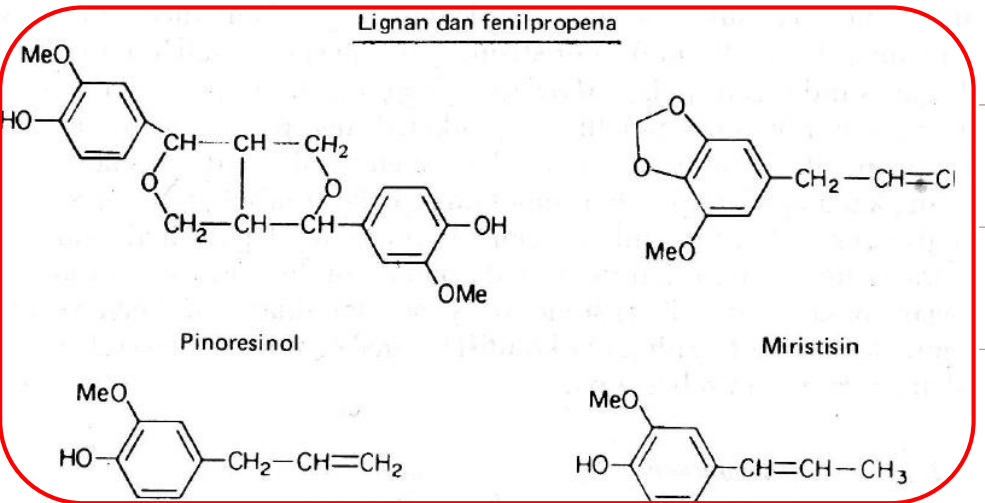
Senyawa ini secara bebas larut dalam pelarut-pelarut organik.

Senyawa ini berada baik sebagai isomer cis maupun trans.

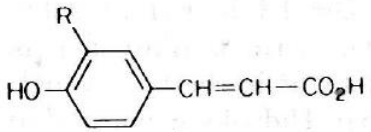




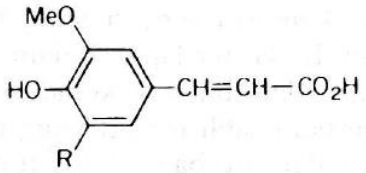




Asam hidroksisinamat

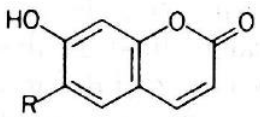


R = H, asam *p*-kumarat
R = OH, asam kafeat

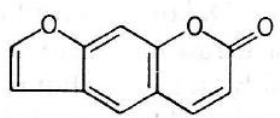


R = H, asam ferulat
R = OMe, asam sinapat

Kumarin

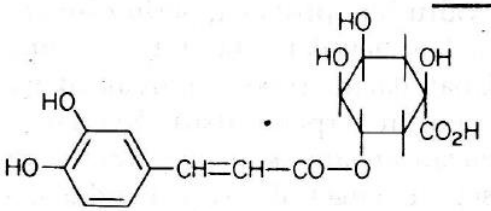


R = H, umbeliferon
R = OH, eskuletin
R = OMe, skopoletin

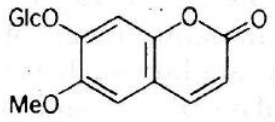


Psoralen

Bentuk terikat

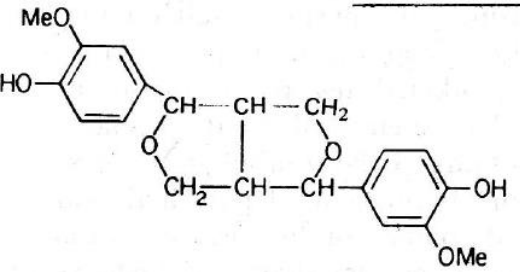


Asam klorogenat

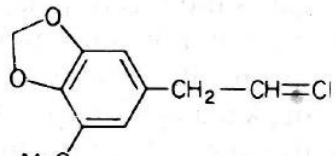


Skopolin

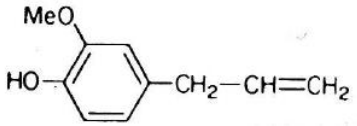
Lignan dan fenilpropena

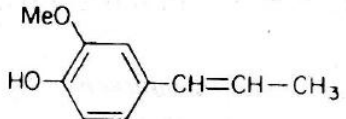


Pinoresinol



Miristisin





2. Turunan kumarin

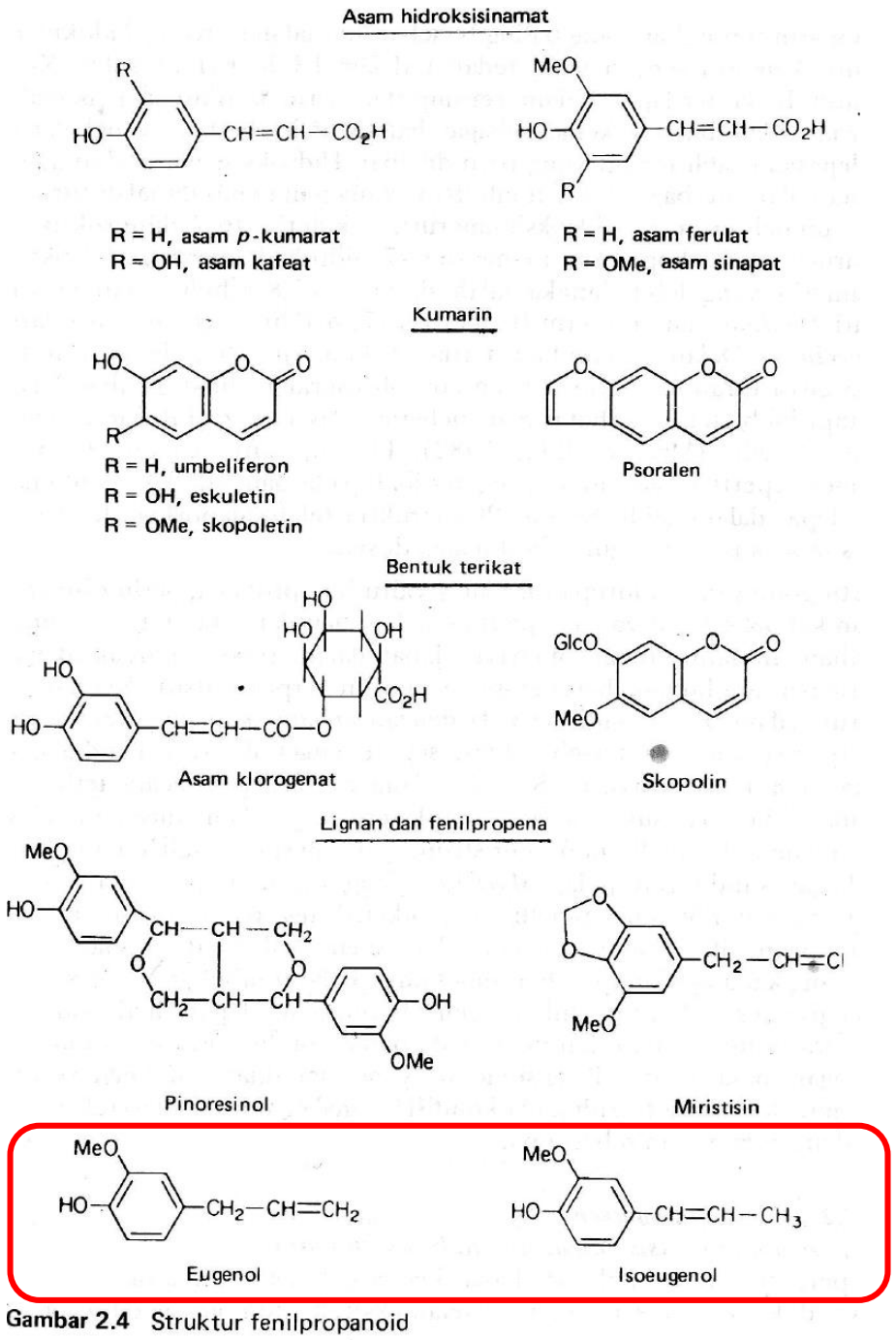
Kumarin dan turunannya adalah senyawa yang sangat reaktif.

Keberadaan gugus metil di posisi C_4 atau C_6 membuat inti kumarin lebih reaktif, dan dapat mengakibatkan inti kumarin menjalani reaksi halogenasi serta kondensasi dengan aldehida.

C_6 pada cincin aromatik dapat mengalami serangan elektrofilik, misalnya sulfonasi atau reaksi asilasi Friedel-Craft.

Sebuah substituen metil pada inti kumarin bereaksi secara berbeda, tergantung pada posisi serangan.

Sebagai contoh, sebuah gugus metil yang terikat pada C_6 atau C_4 lebih reaktif dari gugus metil di posisi C_3 atau C_5.



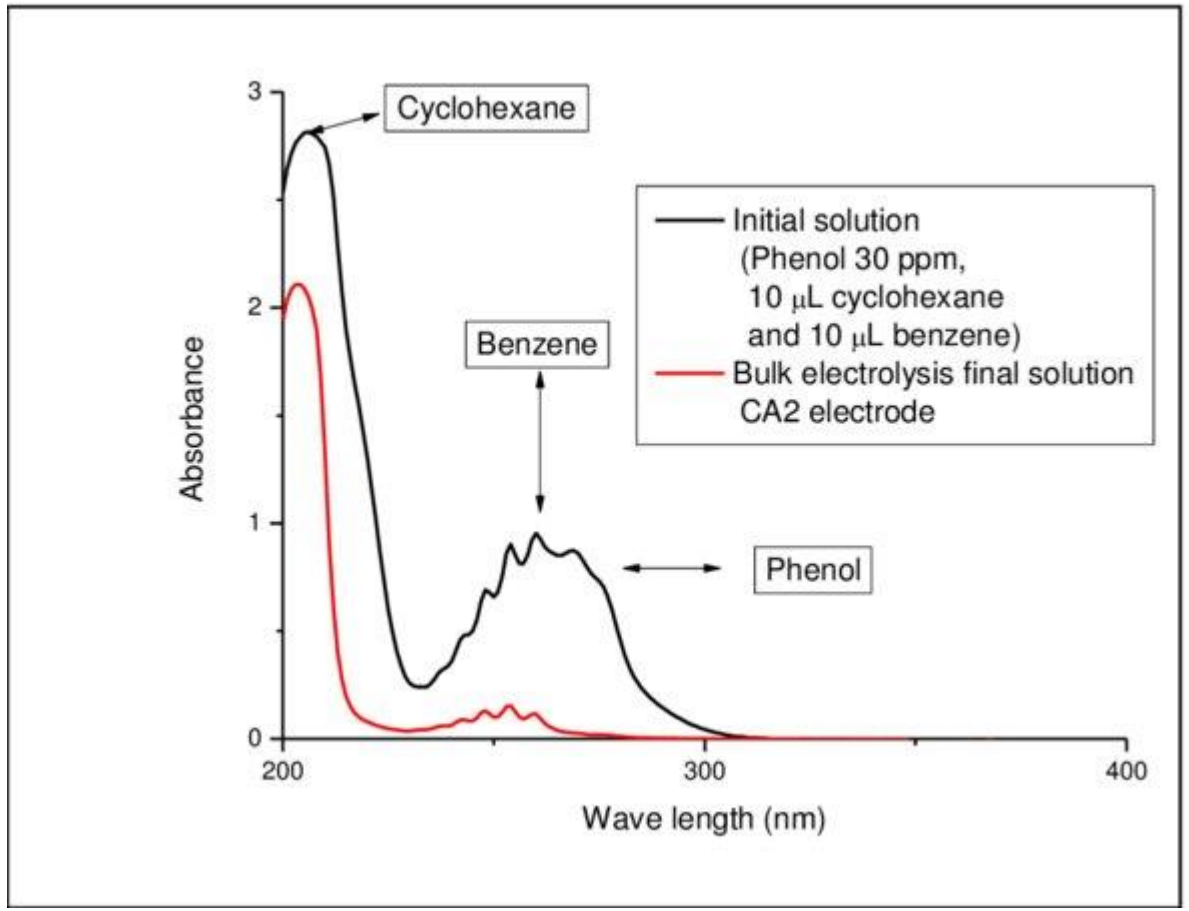
Gambar 2.4 Struktur fenilpropanoid

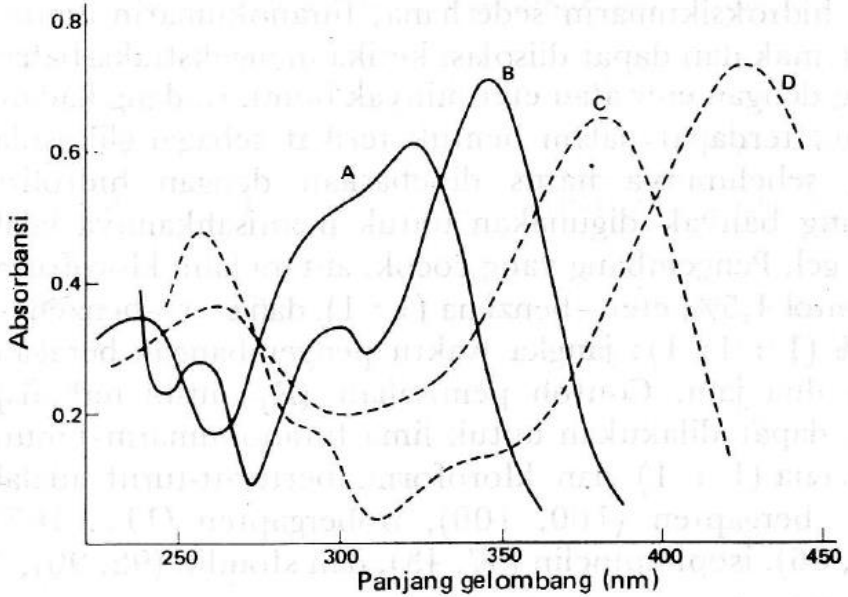
3. Turunan alilfenol

- Senyawa-senyawa alilfenol dan propenilfenol adalah dua jenis senyawa fenilpropanoida yang berkaitan satu sama lainnya.
- Senyawa-senyawa ini umumnya ditemukan bersama-sama dalam minyak atsiri dari tumbuhan umbeliferae atau tumbuhan lain yang digunakan sebagai rempah-rempah.

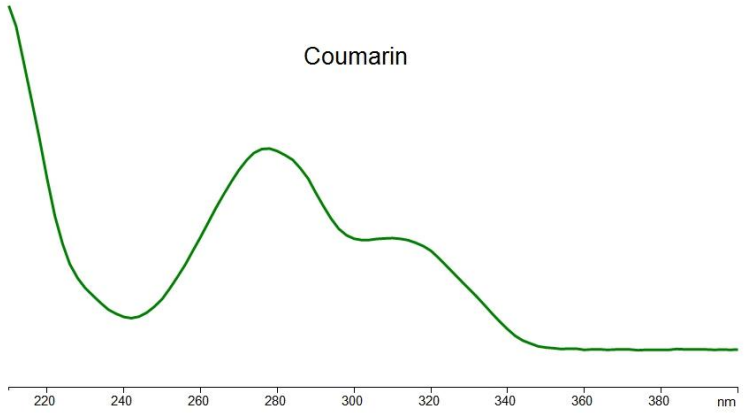
4. Turunan propenil Fenol

Spektrum UV





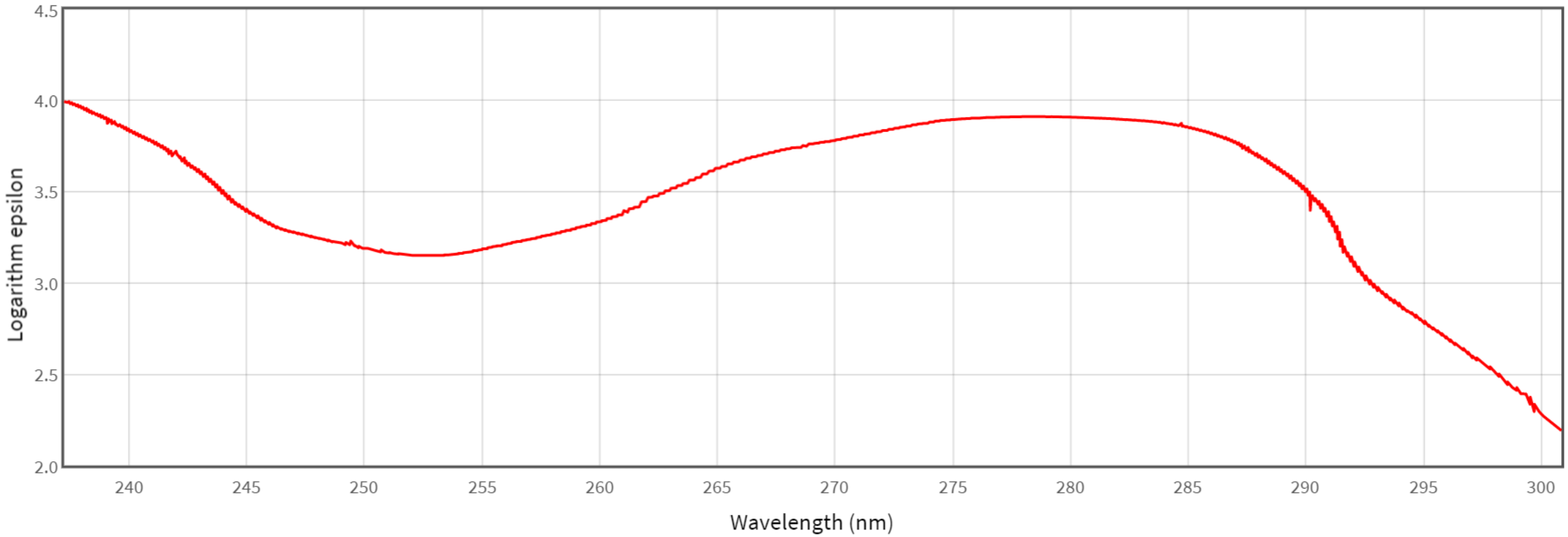
Gambar 2.6 Spektrum ultraviolet dua fenilpropanoid. Keterangan: A = asam kafeoilkuinat (asam klorogenat) dalam EtOH 95%; B = eskuletin dalam EtOH 95%; C = asam kafeoilkuinat dalam EtOH-NaOH; D = eskuletin dalam EtOH-NaOH.



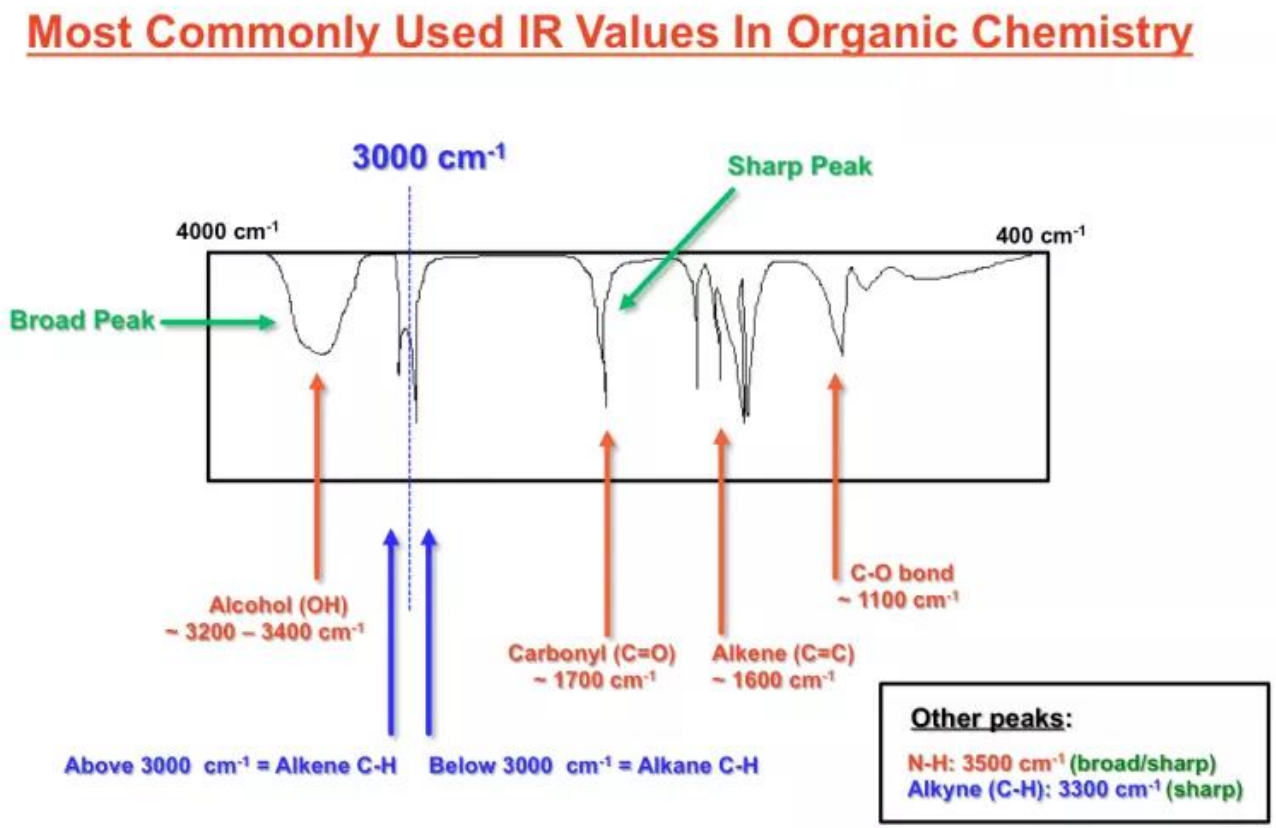
Plot | Help / Software credits

Eugenol

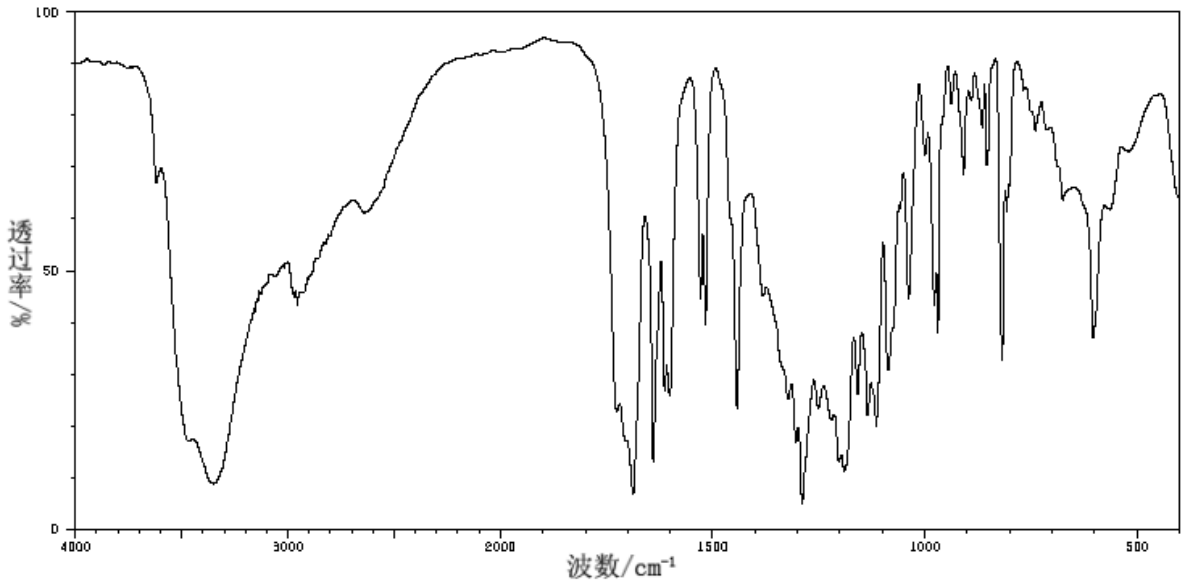
Uv/vis Spectrum



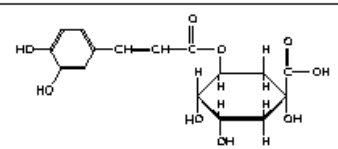
IR Spektrum

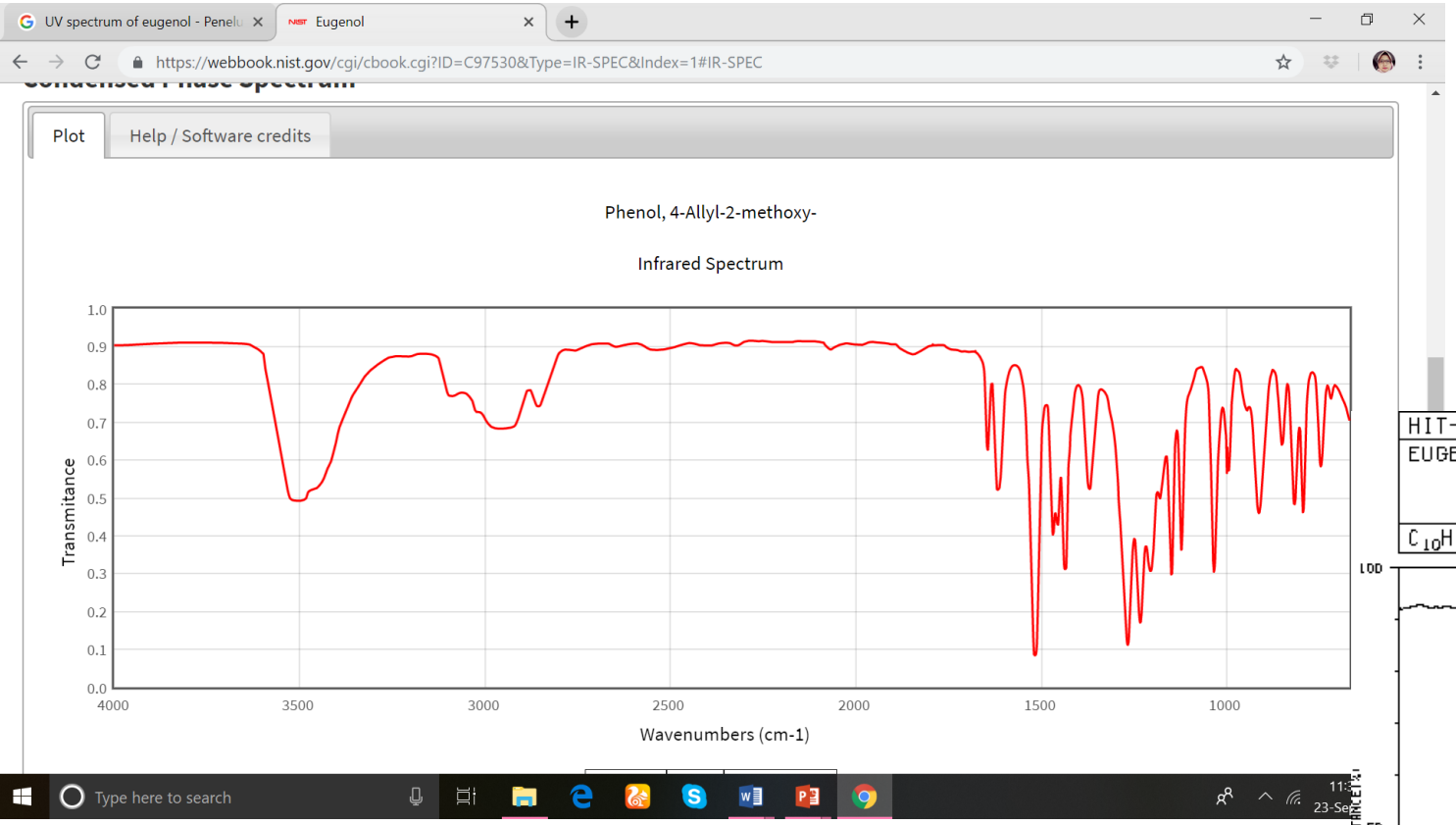


Asam klorogenat

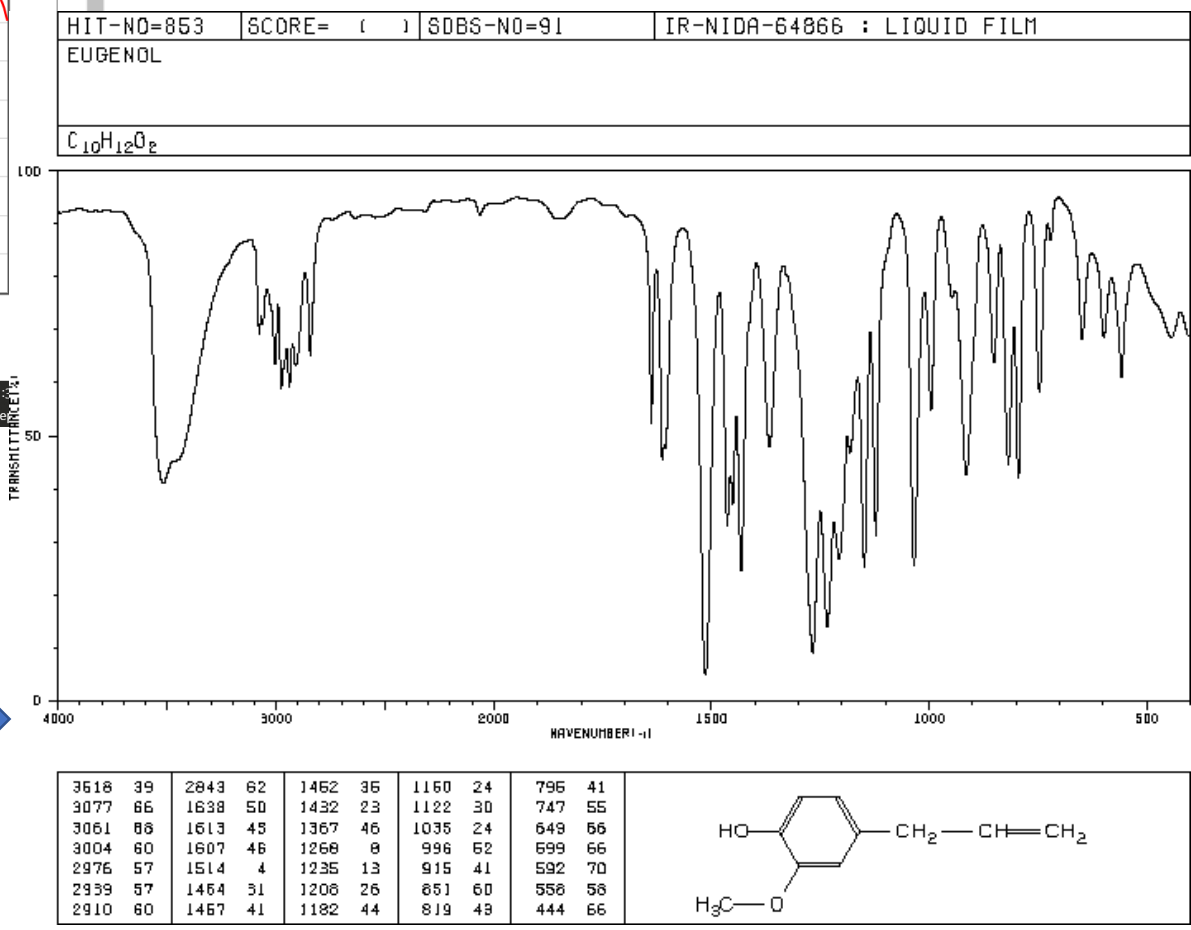


3351	8	1687	6	1382	43	1191	10	969	37
2971	43	1640	13	1323	24	1159	25	818	32
2953	42	1613	26	1304	16	1135	21	807	58
2932	44	1601	26	1289	4	1114	19	801	64
2840	58	1529	43	1251	23	1086	30	676	62
1726	22	1518	38	1221	20	1038	49	604	36
1705	16	1443	29	1203	13	978	42	564	60





Hasil cek pada data base www.nist.gov



Hasil pengukuran

3518	39	2843	62	1462	36	1160	24	796	41
3077	66	1638	50	1432	23	1122	30	747	55
3061	68	1613	45	1367	46	1035	24	649	66
3004	60	1607	46	1268	8	996	52	599	66
2976	57	1514	4	1235	13	915	41	592	70
2939	57	1464	31	1208	26	851	60	556	58
2910	60	1467	41	1182	44	819	43	444	66

Contoh isolasi :
Eugenol, eugenol asetat dari bunga cengkeh

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Original Article

ANTIFUNGAL *PHYTOPHTHORA PALMIVORA* FROM CLOVE BUDS (*SYZYGIUM AROMATICUM* L.)

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Extraction and fractionation

Clove buds powder (500 g) was macerated successively at room temperature using n-hexane, ethylacetate and methanol (4 l) for3x24hrespectively. Each extract was evaporated using arotary evaporator at 50°C. Isolation of clove oil was performed by steam distillation using 40 gclove powders. The extract and clove oilwere tested for the antifungal activity. Analytical Thin-Layer Chromatography (TLC) was performed on precoated silica gel 60 GF_{254} plate (Merck). The spots of each extract and the essential oil were compared with eugenolauthentic marker (Sigma-Aldrich) and visualized under UV light and by spraying with p-anisaldehide-sulfuric acid reagent. The n-hexane extract (20 g) was separated on vacuum liquid chromatography (13 x 10 cm); packed with 200 g Kiesel gel 60 H, 10-40 µm mesh (Merck), eluted with gradient elution using a combination of n-hexane and ethyl acetate to give seven fractions named F1-F7. Each fraction was tested for the antifungal activity.

Fraction F2 was chromatographed on column (2.0 x 45 cm) packed with 25 g Kiesel gel 60 (Merck), eluted withn-hexane to give eight fractions named F2A-F2G. Fraction F2A was further chromatographed on column (2.0 x 45 cm) packed with 20 g Kiesel gel 60 (Merck) eluted with n-hexane to give nine sub fractions named F2A. A-F2A. I. Fraction F2A. E was chromatographed on column (2.0 x 45 cm) packed with 15 g Kiesel gel 60 (Merck) eluted withn-hexane to give ten sub fractions named F2A. E1-F2A. E10. Each sub fraction was tested for antifungal activity. Fraction F5 was separated on vacuum liquid chromatography (9 x 17 cm) packed with 100 g Kiesel gel 60 H (Merck) eluted with n-hexane and ethyl acetate to give seven fractions named F5A-F5G. Fraction F5Ewas chromatographed on the column (2.0 x 45 cm) packed with 30 g Kiesel gel 60 (Merck) eluted n-hexane and ethyl acetate to give eight sub fractions named F5E.1-F5E.8. Each subfraction was tested for the antifungal activity.

Simplisia Cengkeh

Ekstraksi

- **E. Hexan** — 18,52 %
- **E. Etil asetat** — 4,748 %
- **E. Metanol** — 14,11 %
- **Minyak atsiri**

K. Cair Vakum

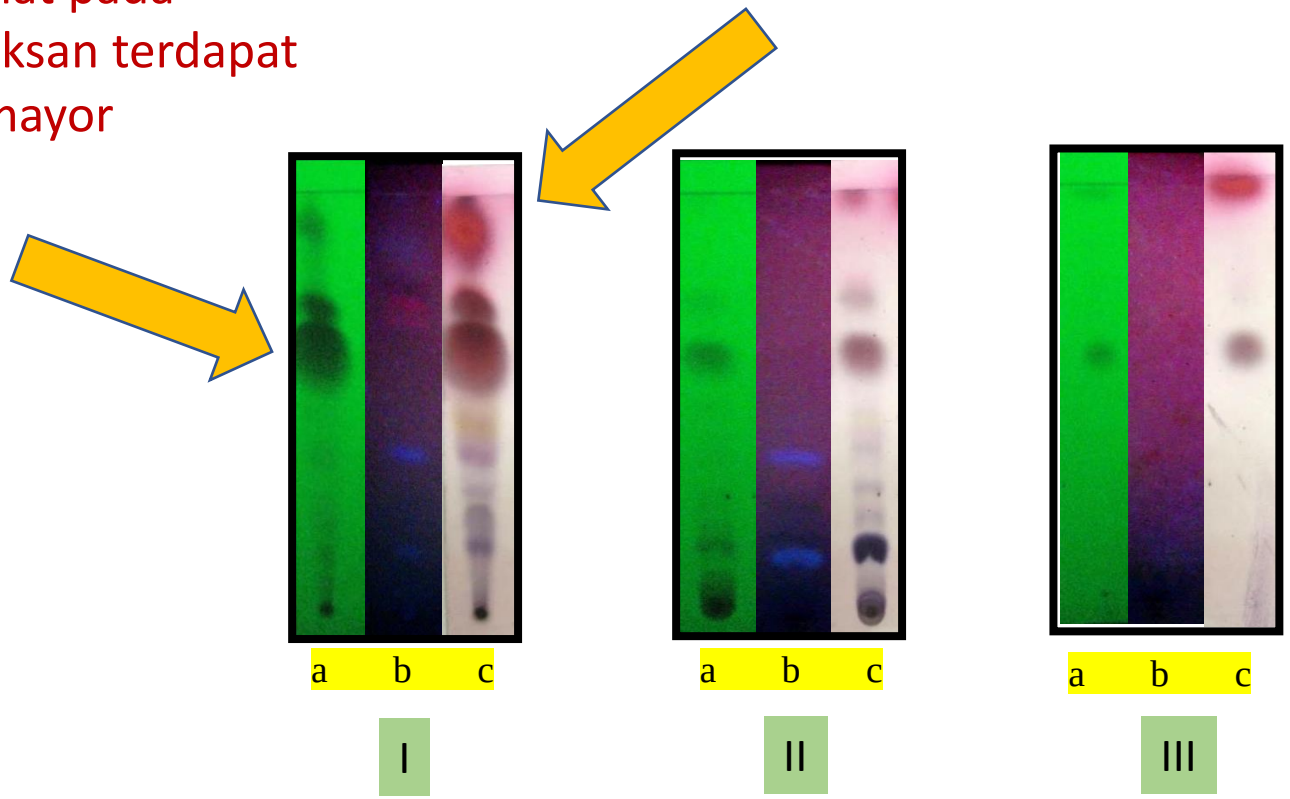
- F.1
- F.2 — 10,15 %
- F.3
- F.4
- F.5 — 74,35 %
- F.6
- F.7

Kromatografi kolom → **Subfraksi 1**

Kromatografi Cair Vakum → **Subfraksi A-G**

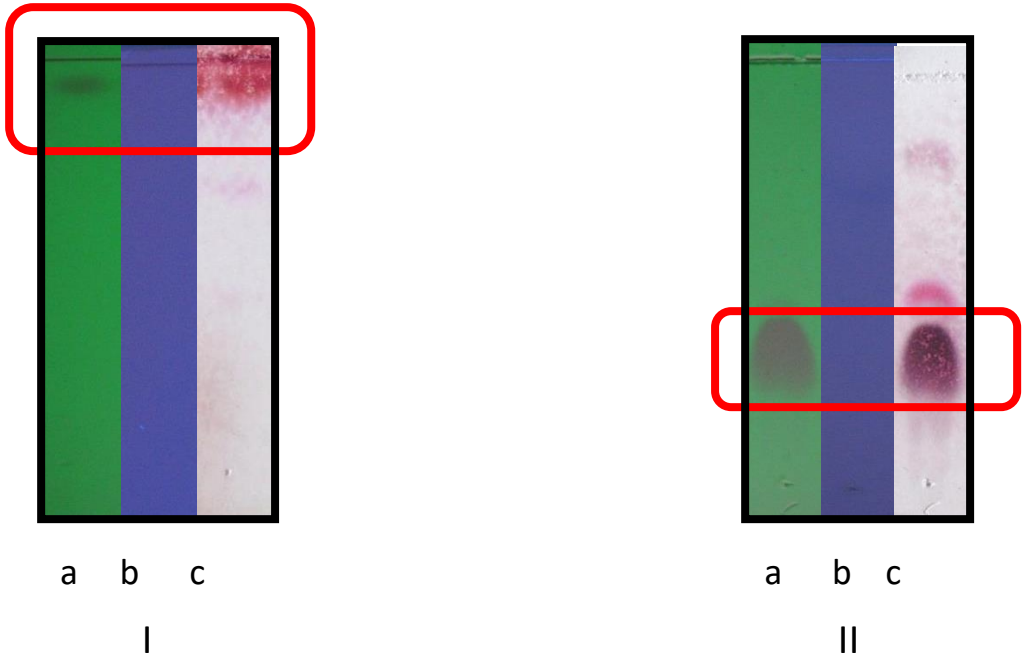
Kromatografi kolom → **Subfraksi 2**

Dapat dilihat pada
ekstrak heksan terdapat
senyawa mayor



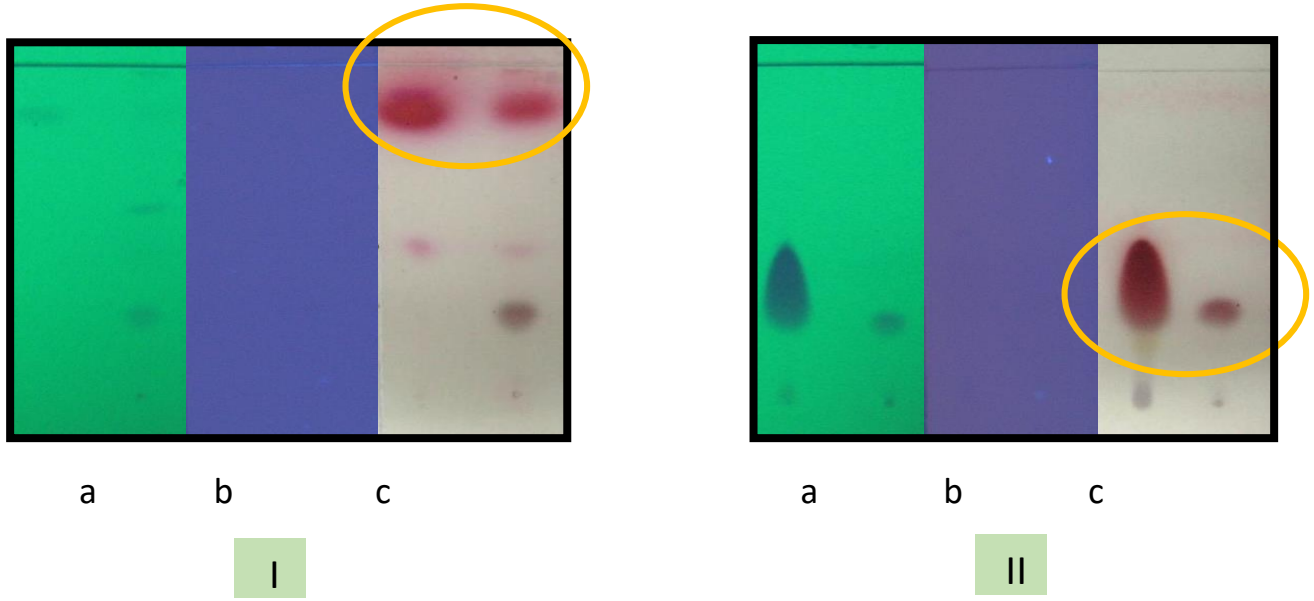
Gambar 1. Kromatogram lapis tipis
fase diam silika gel F254 , fase gerak Toluen-aseton (9:1),
(I) ekstrak heksan, (II) ekstrak etil asetat, (III) minyak atsiri,
(a) UV 254nm, (b) UV 366nm, (c) anisaldehid-as.sulfat, dipanaskan.

Hasil fraksinasi menggunakan K. Cair Vakum



Gambar 3. Kromatogram lapis tipis
fase diam silika gel F254 , fase gerak heksan-etil asetat (9:1),
(I) fraksi 2, (II) fraksi 5,
(a) UV 254nm, (b) UV 366nm, (c) anisaldehid-as.sulfat, dipanaskan.

Hasil subfraksinasi menggunakan K. Kolom



Gambar 4. Kromatogram lapis tipis fase diam silika gel F254 , fase gerak heksan-etil asetat (9:1), **(I) subfraksi 1 dengan pembanding minyak atsiri, (II) subfraksi 2 dengan pembanding eugenol standar,** (a) UV 254nm, (b) UV 366nm, (c) anisaldehid-as.sulfat, dipanaskan.

Sub fraction F-A

Sub fraction F-A, collected from fraction F2, was clear and aromatic oil. It was predicted as components of clove oil, based on TLC chromatogram compared with the clove oil (purchased from Manoko, West Java, Indonesia). The subfraction F-A gave pink spot with Rf value 0.85 using n-hexane-ethyl acetate (9:1) and anisaldehide-sulfuricacid as spray reagent. The chromatogram of gas chromatography showed the main peak (F-A) the major component at 80.52% based on the peak area and few minor peaks. The main peak F-A (fig. 3) has retention time 12 minutes with m/z 133 [M^+] 204 in EI-MSwithamolecular formula $C_{15}H_{24}$and identified as caryophyllene (bicyclic sesquiterpene).

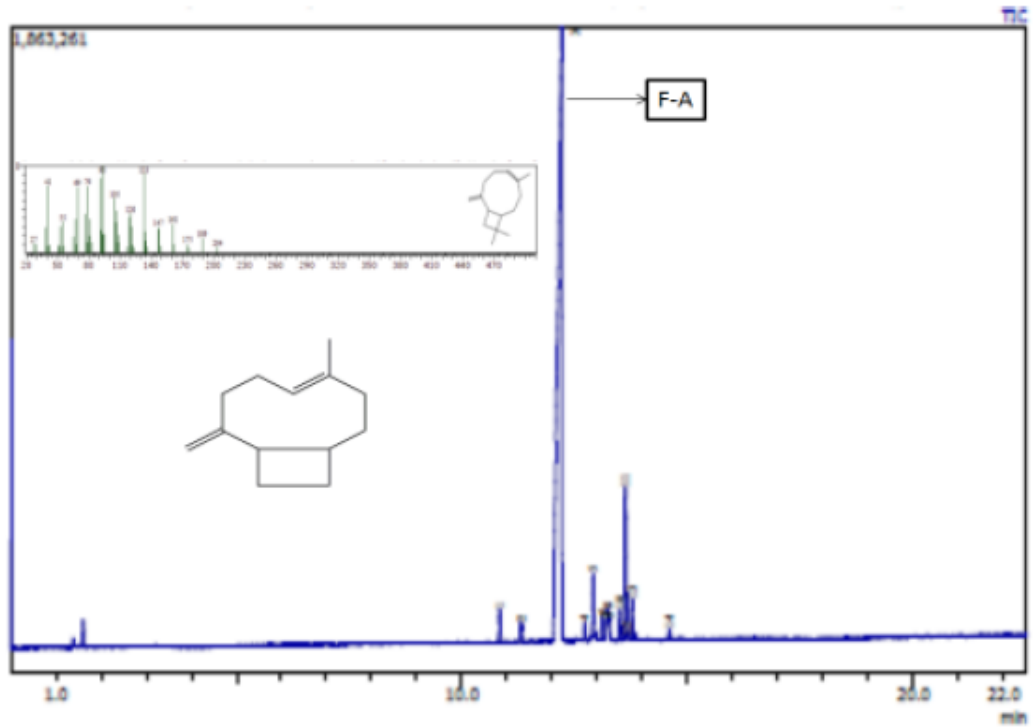
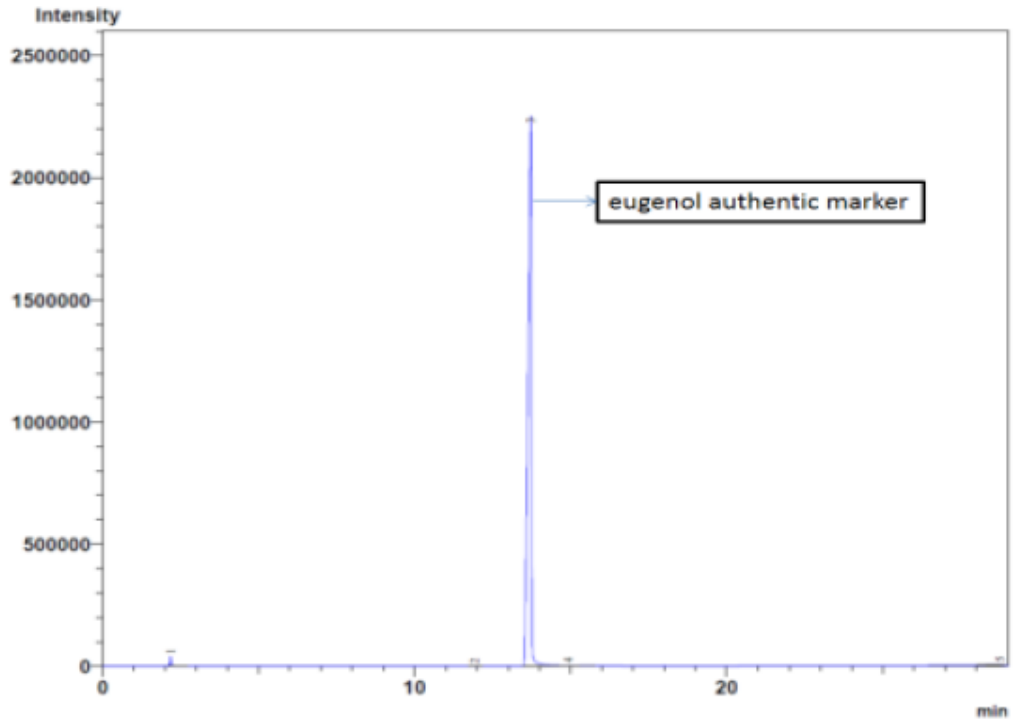


Fig. 2: GC-MS chromatogram major peak of sub fraction F-A (caryophyllene)

Sub fraction F-B

Sub fraction F-Bwas collected from fraction F5. It was clear, pale yellow, aromatic, leaved warm in hand. One of the components was identified as eugenol after comparison with eugenolauthentic marker (Sigma-Aldrich). The Rf value was 0.35 on TLC using (n-hexane-ethyl acetate (9:1) as solvent and anisaldehide-sulfuric acid as spray reagent. Analysis by GC-FID gave two main peaks F-B1 and F-B2 (fig. 3). The peak F-B1 has retention time 13.7 minutes, same with eugenolauthentic marker while F-B2 at 11 minutes. The peak F-B1 has m/z 164, [M^+] in EI-MS with a molecular formula $C_{10}H_{12}O_2$ and identified as eugenol. The peak F-B2 has m/z 206, [M^+] in EI-MS with a molecular formula $C_{12}H_{14}O_3$and identified as acetyl eugenol.



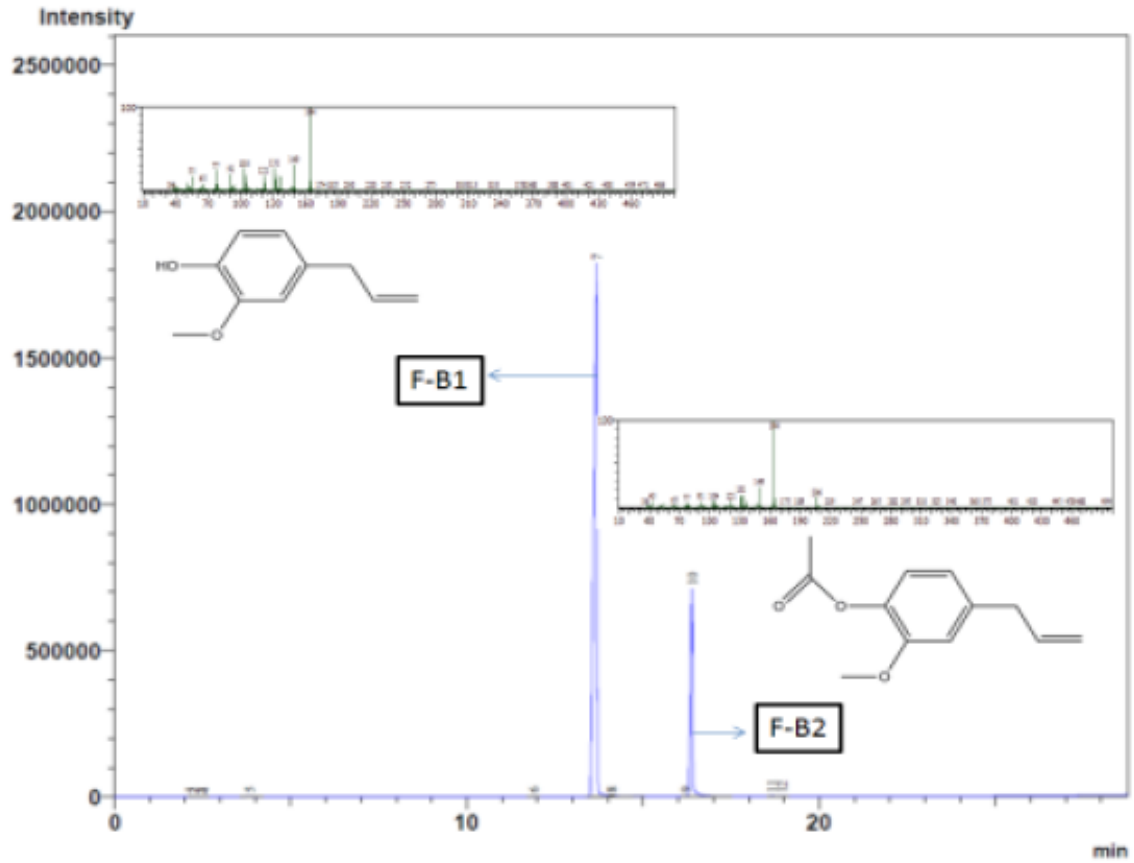


Fig. 3: GC-MS chromatogram major peak of sub fraction F-B1 (eugenol) and F-B2 (eugenol acetate)