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Chemical constituents from the bark of *Lannea acida* Rich (Anacardiaceae)

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ABSTRACT

Four flavonoids named as 6,7-(2",2"-dimethyl chromeno)-8-γ,γ-dimethyl allyl flavanone, 3',4'dihydroxy-7,8 (2",2"-dimethyl chromeno)-6-γ,γ dimethyl allyl flavonol, 7-methyltectorigenin, Irisolidone, have been isolated from leaves of Lannea acida . Their structures were elucidated by chemical and physical data (IR, UV, ^{1}H-NMR, and Mass spectra).

Keywords: *Lannea acida* ; flavonoids.

INTRODUCTION

Lannea acida (syn. Odina acida) a small deciduous tree, leaves excee-ding 30 cm. It is used as an important drug of the indigenous system of treatment in North Nigeria. The leaves and bark are used as febrifuge and have been described to be useful in gout, rheumatism, for wounds, swelling and burns[1]. A survey of the literature showed that no work has been reported on the bark of this medicinally important plant[2], therefore the present discussion deals with the isolation and characterization of the following compounds from the bark of *Lannea acida* .

1) 6,7-(2",2"-dimethyl chromeno)-8-γ,γ-dimethyl allyl flavanone.
2) 3',4'dihydroxy-7,8 (2",2"-dimethyl chromeno)-6-γ,γ dimethyl allyl flavonol.
3) 7-methyltectorigenin.
4) Irisolidone.

MATERIALS AND METHODS

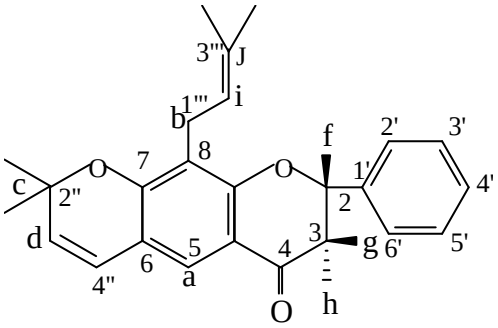
Coarsely powdered bark (1 Kg) was exhaustively extracted with acetone. The acetone concentrate was successively extracted with petroleum ether, chloroform and finally with ethylacetate. The chloroform and ethyl-acetate concentrates gave positive tests for flavonoids.[3-6] On TLC examination these concentrates showed four major spots in BPF and TEF, with the same R_f values. The above two concentrates were therefore mixed together. Repeated column chromatography over silica gel followed by fractional crystallization afforded four crystalline TLC homogeneous substances. They were given the labels as **La-1, La-2, La-3 and La-4** in order of their increasing R_f values.

RESULTS AND DISCUSSION

La-1:

La-1 was eluted from the column by benzene-ethylacetate (3:1) mixture. On crystallization from benzene-ethylacetate it gave colourless needles m.p. 92^{0}C. Elemental analysis and the molecular ion peak at m/z 374 agreed with the molecular formula $C_{25}H_{26}O_3$. A pink colour with magnesium and hydrochloric acid and a blue colour on treatment with sodium amalgam followed by acidification, suggested a flavanone nucleus for the compound.[7] In its **^{1}H-nmr** spectrum two protons (C_3–2H) multiplet centered around δ 3.0 and a one proton (C_2–H) multiplet centered around δ 5.15, clearly defines **La-1** as a flavanone.

The **^{1}H-nmr** spectrum of **La-1** showed the presence of a γ,γ-dimethyl allyl unit and 2",2"dimethyl chromene ring. The singlet at δ 1.46 (c) for six protons and two olefinic doublets at δ 4.4(e) and 3.4(d) with Jde 11 Hz signify the dimethyl chromene ring. The two three protons singlets at δ 1.75 and 1.8 (J) and the doublet at δ 3.2 (b) (J=7 Hz) for two protons and an olefinic triplet, at δ 5.4 (i) (J=7 Hz) revealed the γ,γ-dimethyl allyl unit. Besides these a sharp singlet at δ 7.5 for five protons (unsubstituted phenyl) and the singlet at δ 7.7(a) for one proton (C_5–H) indicated that the compound has a trisubstituted. Ring-A having the chromene as well as the dimethyl allyl unit and the unsubstituted side phenyl.



(I)

On the basis of the findings of the **^{1}H-nmr** spectrum. **La-1** was assigned the structure as **6,7-(2",2"dimethyl chromeno)-8-γ,γ-dimethyl allyl flavanone (I).**

In the **^{1}H-nmr** spectrum**,** the chromanone ring hydrogens f.g and h showed the signals centered at δ 5.35, 2.8 and 3.0 respectively, coupling constant J gh 18, J fh 15 and J f g 4 Hz.

The **mass** spectrum of **La-1** showed a molecular ion peak at m/z 374 (10%). The base peak appears at m/z 55. The **(scheme-I)** outlines the pattern of fragmentation. The, peak at m/z 359 belong to the ion arising by the loss of one of the methyl groups at chromene ring. A peak at m/z 319 showed the loss of C_4H_{17}. This is in analogy with the cleavage of the side chain as scandenone-4-methyl ether.[8]

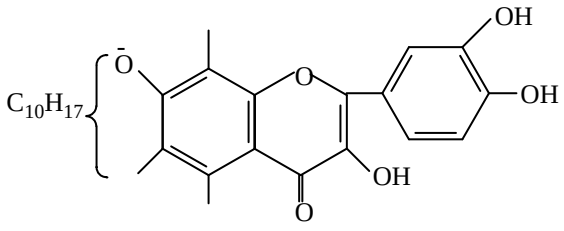
La-2:

The fraction **La-2** was eluted with benzene-ethylacetate mixture (1:1). Recovery of the solvent left a residue, which was crystallized from methanol as yellow needles, m.p.165^{0}C. Elemental analysis suggested $C_{25}H_{24}O_6$ as the molecular formula of the compound, further confirmed by the molecular ion peak at m/z 420.

The **uv** and **ir** spectra of **La-2** and its derivatives showed that it cont-ained a conjugated carbonyl group and three phenolic hydroxyl groups. It gave green colour with ferric chloride. A pink colour with magnesium and hydrochloric acid[9] and a bright yellow colour with Wilson-boric acid reagent[10] showed it to be a flavonol. A flavonol structure was evidenced further with the **uv** data for **La-2** and its derivatives and with the marked dependence of the **ultra-violet** spectrum of **La-2** upon solvent and pH.[11] A 20 nm red shift of Band I in the presence of $NaOAc/H_3BO_3$ indicated the presence of ortho- dihydroxy group. Alkaline fusion gave 3,4-dihydroxybenzoic acid.

Assuming a flavonol structure for **La-2**, five oxygen atoms were thus accounted for, two belonging to the γ-pyrone ring and three to phenolic hydr-oxyl groups. This led to the proposal of the partial structure (II-a). On biog-enetic grounds and by inspection of the **uv** data, the sixth oxygen was placed in position 7.

Biosynthetic argument suggest that the $C_{10}H_{17}$ residue in **(II-a)** may consist of two isoprene units[12] (C_5H_8+ C_5H_9).

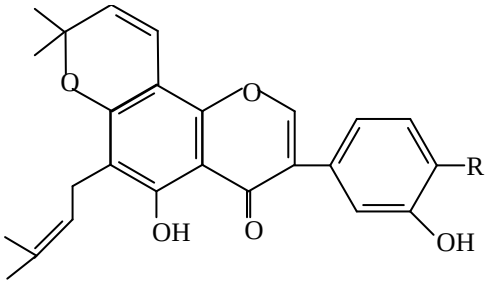


(II-a)

La-2 and its derivatives showed absorption in the 222-230 nm region which is characteristic of 2",2"dimethyl chromene. Kuhn-Roth oxidation of **La-2** gave 1.25 equivalent of acetic acid, which suggested two Me_2C units. Thus the C_5H_9 unit could be located in a 2",2"-dimethyl chromene residue and a C_5H_9 unit could exist as a CMe_2: CH-CH_2 group.

Following structure (II) was tentatively proposed [cf[8] osajin (II-b) & pomiferin (II-c)].

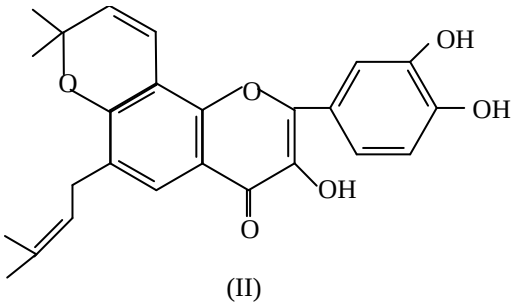
The **^{1}H-nmr** spectrum of the acetate of **La-2** exhibited a singlet at δ 1.4 for six protons, two doublets at δ 5.8 and 6.7 (J=10 Hz) signifying the dimethyl chromene ring. Two singlets for three protons each at δ 1.8 and 1.9, doublet at 3.4 (J=7 Hz) for two protons and an olefinic proton multiplet at δ 5.2 revealed the γ,γ-dimethylallyl unit.[13,14,15] In addition the spectrum showed one proton singlet at δ 7.9 ascribable to C_5–H.



II-b: R = H
II-c: R = OH

On the basis of above data, **La-2** was assigned the structure as **3',4' dihydroxy-7, 8-(2",2"-dimethyl chromeno)-6-γ,γ-dimethy allyl flavonol (II)**.

La-3:
Fraction **La-3** was obtained from benzene-ethylacetate mixture (1:3) and crystallized as yellow needles from methanol. The molecular ion peak at m/z 314 and elemental analysis point the molecular formula as $C_{17}H_{14}O_6$ Micro- Zeisel determination showed the presence of two methoxyl groups. The presence of two free hydroxyl groups was confirmed by the formation of diacetate and dimethyl ether of the compound **La-3**.

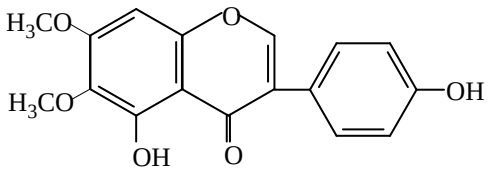


(II)

It gave pink colouration on treatment with sodium amalgam followed by acidification with HCl. The **uv** spectrum showed λ_{max} at 268 nm and an infle-ction at 334 nm. The molecular formula, positive colour test with sodium amalgam and **uv** absorption suggest it to be an isoflavone, further confirmed by the **^{1}H-nmr** in which the signlet of the C-2 proton appeared at about δ 7.8. A dark green colour with ferric chloride[16] and a band at 3450 cm^{-1} in **ir** spectrum showed the presence of chelated hydroxyl group, further confirmed by a red shift of 12 nm in the **uv** spectrum on addition of anhydrous aluminum chloride.

The formation of di-acetate and dimethyl ether, along with the molecular formula and **uv** spectra suggest that the compound is an isoflavone with two methoxyl and two hydroxyl groups. The methanolic solution of the compound was not oxidised by pentamine cobalttrichloride, indicating the absence of adjacent phenolic hydroxlic groups. One of the hydroxyl group, was placed at C-5. In the **^{1}H-nmr** spectrum the aromatic region contains multiplets of four protons of ring B. A multiplet and a doublet centered at δ 6.9 and 7.4 respectively corresponds to an A_2B_2 pattern, the remaining hydroxyl group was placed at C-4', which funds by mass fragmentation.

In the **^{1}H-nmr** spectrum a sharp singlet at δ 7.8 indicated the presence of C-2 proton of γ-pyrone nucleus. The presence of two methoxyl groups, was indicated through two singlets at δ 3.92 and 3.96 for three protons each. A singlet at δ 6.46 integrating for one proton can be assigned to an aromatic proton shielded by two ortho and one paraoxygen. It can arise from the C-6 proton of a 5,7,8-trioxygenated isoflavone or the C-8 proton of 5,6,7-tri oxygenated isoflavone. The methoxyl has been put at 6-position on the evidence of **mass** spectrum, thus assigning the singlet at δ 6.46 to C-8 proton.



(III)

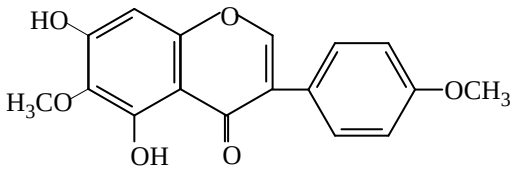
The compound **La-3** was characterized as **7-methyl tectorigenin (III)** by its melting and mixed melting points with an authentic sample of 7-methyl-tectorigenin and its acetate.[17] Further conformation to its identify was furnished by spectral evidences.

The **mass** spectrum showed $M^{+\cdot}$ at m/z 314 and $M^{+\cdot}$–15 corres-ponding to the loss of methyl, at m/z 299.$M^{+\cdot}$ is 100% and $M^{+\cdot}$–15 peak is about 70%. This is extremely significant and provides the justification for putting the methoxyl at C-6 for in 8-methoxy 5-hydroxy flavonoids the order is reversed and the predominnt peak is that resulting from the loss of methyl from $M^{+\cdot}$. Peak at m/z 118 suggested it due to p-hydroxyphenylacetylene ion indicating mono oxygenation in ring-B **(scheme-II)**. Ring-A (RDA) fragment expected at 196 is not found but peak at m/z 153 might be coming from 196 by loss of CO.

La-4:

La-4 was eluted from the column by benzene-ethylacetate (1:15) mix-ture. It gave the characteristic colour reactions of isoflavones[10,18].The **uv** absorption spectrum was similar to that of irosolone and tri-O-methyl-tectori-genin.[14] The elemental analysis showed a molecular formula $C_{17}H_{14}O_6$ and two methoxyl groups. A blue colour with ferric chloride and formation of diacetate and dimethyl ether showed the presence of two free hydroxyl groups. Specific colour reaction further indicated that one of these must be located in the 5-position and the vicinal hydroxyl groups were not present. A red shift of 10 nm in the **uv** spectrum characteristic of 5-hydroxyl was observed on addition of aqueous aluminum chloride[19,20] and a similar shift of 8 nm on addition of fused sodium acetate suggested a 7-hydroxyl group.

The **^{1}H-nmr** showed a sharp singlet at δ 7.9 for one proton characteristic of the H-2 of the isoflavone. Two singlets at δ 3.8 (3H) and 3.9 (3H) indicated the presence of two methoxyl groups. Examination of the aromatic protons region showed the typical A_2B_2 pattern by a doublet centered at δ 6.9 (J=10 Hz) and another centered at δ 7.5 (J=10 Hz), each integrating for two protons, thus showing 4'-oxygenation with side phenyl. A singlet at δ 6.5 (1H) may be assigned to H-8. Thus the compound **La-4** appeared to be a dimethyl ether of 5, 6, 7, 4'-tetrahydroxy isoflavone.
The spectral evidence showed the compound to be **irisolidone**[21] (IV) further confirmed by a comparison of its **uv** and **ir** with an authentic sample of irisolidane and by co-TLC and mixed melting point.



(IV)

CONCLUSION

Extraction and isolation

Coarsely powdered bark (1 Kg) was exhaustively extracted (3 times, 5 liters each) by refluxing with acetone. All the acetone extracts were combined together and distilled under reduced pressure. A dark brown syrupy mass was left behind. The residue was successively extracted with petroleum ether (60-80^0), chloroform and finally with

ethylacetate. The chloroform and ethylacetate concentrates on TLC examination in BPF and TEF systems showed four major spots with the same R_f values and shad in **uv** light. The above two concentrates were therefore mixed together. The combined extract (23 gm) was subjected to column chromatography over silica gel (2.5 Kg) and eluted with benzene-ethylacetate in different proportions, monitored by TLC. Fractions each of 50 ml, were collected and the following compounds were isolated from different pools of identical fractions **, La–1 (435 mg), La–2 (350 mg), La–3(250 mg) and La–4 (270 mg).**

La–1:
The benzene-ethylacetate (3:1) fractions of the column were found identical on TLC and therefore pooled together. Removal of the solvent by distillation under reduced pressure gave a gummy mass. The gummy mass (7 gm) was dissolved in a small quantity of acetone and mixed with silica gal. The slurry was loaded on a column of silica gel (60 g / 100-200 mesh; 42 x 3.0 cms) and successively eluted with petroleum ether and benzene and finally with benzene-ethylacetate (95:5) and (9:1) mixture. Fractions eluted with benzene-ethylacetate mixture showing single spot on TLC examination were combined together and on concentration gave a dirty white solid which was crystallized from benzene-ethylacetate as white needles melting point 92^0C. λ^{EtoH}_{max} nm (E x 10^{-3}) : 222 (25.5), 272 (14.6). Analysed for $C_{25}H_{26}O_3$: Calcd.: C, 80.21; H, 6.95%, Found: C, 80.14; H, 6.97%

^{1}H-NMR (60MHz, $CDCl_3$) on δ scale : 1.5 (6H, s, >C $(CH_3)_2$), 1.75, 1.8 (2x3H, s, >C $(CH_3)_2$), 3.2 (2H, d, J=7 Hz,-CH–), 5.4 (1H, t, =CH–), 5.6, 6.7 (2x1H, d, J=11 Hz -CH = CH-), 7.5 (5H, s, 2',3',4',5'-H), 7.7 (1H, s, 5-H), 3.0 (2H, m, 3–H), 5.15 (1H, m, 2–H).

Mass, m/z: $M^{+\cdot}$ 374 (10%), 55, 359, 319.

Chalcone: La-1 (100 mg) was suspended in water (10 ml) and a slow current of nitrogen free from oxygen was passed through the suspension. After 5 minutes aqueous sodium hydroxide (5 ml, 10%) was added, and the mixture was heated over a boiling-water bath for 30 minutes, cooled to room temperature, acidified with hydrochloric acid, and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated. The yellow residue was crystallized from ethyl-acetate melting point 125-26^0C. Analysed for $C_{25}H_{24}O_3$: Calcd.: C, 80.64; H, 6.45%, Found: C, 80.75; H, 6.49%.

La-2:
It was crystallized from methanol as yellow needles, m.p. 165^0C.

Analysed for $C_{25}H_{24}O_6$: Calcd: C, 71.42; H, 5.71%, found: C, 7.44; H, 575%

UV, λ_{max}: MeOH: 225, 295, NaOAc/H_3BO_3: 225, 314

IR, υ^{kBr}_{max} cm^{-1}: 1632, 1597, 1563, 1494, 1375, 1361, 1123, 896

Mass, m/z: $M^{+\cdot}$ at 420 (40%), 405 (5%), 377 (15%), 365 (5%).

Acetylation of La-2: La-2 (50 mg), acetic anhydride (1.5 ml) and pyridine (1.5 ml) were refluxed for 3 hours. After cooling, the mixture was poured on crushed ice and left overnight. The solid was collected, washed with water and dried. On several crystallization from ethylacetate it gave shining colourless needles, m.p. 120-21^0C. Analyed for $C_{31}H_{30}O_9$: Calcd.: C, 80.13; H, 5.49%, Found: C, 68.45; H, 5.68%.

^{1}H-NMR ($CDCl_3$ + DMSO-d_6) on δ scale: 1.45 (s, 6H, chromene methyls), 1.8 (s, 3H), 1.9 (s, 3H) (methyl group on double bond), 3.4 (d, J=7 Hz, benzylic methylene), 2.3 (s, 6H), 2.5 (s, 3H) (acetoxyls), 5.18 (m, 1H, olefinic proton), 5.8 (d, 1H, J=10 Hz, chromene proton), 6.7 (d, 1H, J=10 Hz, chromene protons), 7.4 (m, 2H, aromatic protons), 6.8 (d, 1H, aromatic proton), 7.9 (s, 1H, C_5–H proton).

Methylation of La-2: La-2 (50 mg), dimethyl sulphate (0.4 ml) anhydrous potassium carbo-nate (0.5 gm) and dry acetone (15 ml) were refluxed over a water bath for 24 hours. The reaction mixture was filtered and the inorganic residue washed several times with hot acetone. On distilling off the solvent, a brown viscous semi solid mass was left behind. It was treated with hot petroleum ether (60-80^0C) to remove unused methyl sulphate. The solid residue on crystallization from chloroform-methyl alcohol gave colourless needles, m.p. 66-68^0C. Analysed for $C_{28}H_{30}O_6$: Calcd.: C, 72.72; H, 6.49; 3-0Me, 20.13%, Found: C, 72.67; H, 6.44; 1-0Me, 19.5%.

La-3:
It was crystallized from methanol as yellow needles, m.p. 236-37^0C.

Analysed for $C_{17}H_{14}O_6$: Calcd: C, 65.0; H, 4.5; OMe, 19.7%, Found: C, 65.23; H, 4.34; OMe, 20.3%.

Uv, λ_{max} nm: EtOH: 268, 334 (inf), $AlCl_3$: 280.

IR, υ^{kBr}_{max} cm^{-1}: 3450 (OH), 1645 (CO) and 1605, 1580, 1515 and 1495 (aromatic).

Mass, m/z: $M^{+\cdot}$ at 314 (100%), 299 (50.8%), 153 (30.6%), 118 (30.5%).

Acetylation of La-3: La-3 (50 mg) was dissolved in pyridine (1.5 ml) and acetic anhydride (1.5 ml) and was added to it. The mixture was heated over boiling water bath for 2 hours. On usual work up and crystallization from methanol it gave colourless needles m.p. 182-84^{0}C. Analysed for $C_{21}H_{18}O_8$: Calcd: C, 63.31; H, 4.52%, Found: C, 6.25; H, 4.49%.

^{1}H-NMR ($CDCl_3$+DMSO) on δ scale: 2.3 (s, 3H, OAc), 2.5 (s, 3H, OAc), 3.8 (s, 3H, OCH_3), 4.0 (s, 3H, OCH_3), 6.8 (s, 1H, C_8 proton), 7.1 (d, 2H, J=9 Hz, 3',5'-H), 7.4 (d, 2H, J=9 Hz, 2',6'–H), 7.8 (s, 1H, H-2).

Methylation of La-3: La-3 (50 mg), dimethyl sulphate (0.4 ml), anhydrous potassium carbonate (0.5 gm) and dry acetone (15 ml) were refluxed for 24 hours over a water bath. After usual work up a greyish precipitate was obtained. The preci-pitate was crystallized from chloroform-methanol mixture as colourless shining crystals (30 mg) m.p. 182-84^{0}C. It showed no depression in melting point on mixing with an authentic sample of tectrogenin trimethyl ether. Analysed for $C_{19}H_{16}O_6$: Calcd: C, 66.66; H, 5.26, Found: C, 66.42; H, 5.21.

La-4:
Fractions obtained from benzene-ethylacetate (1:15) eluate were pooled together, and evaporated to dryness. The yellow solid obtained, on several crystallization from methanol gave light yellow shining needles, m.p. 192-93^{0}C. It gave blue colour with ferric chloride, positive test with boric acid, boric acid in acetic anhydride (dimorth reagent) and negative test with sodium amalgam. Analysed for $C_{17}H_{14}O_6$: Calcd.: C, 64.96; H, 4.45; OMe, 19.14%, Found: C, 64.45; H, 4.39; Ome, 19.28%.

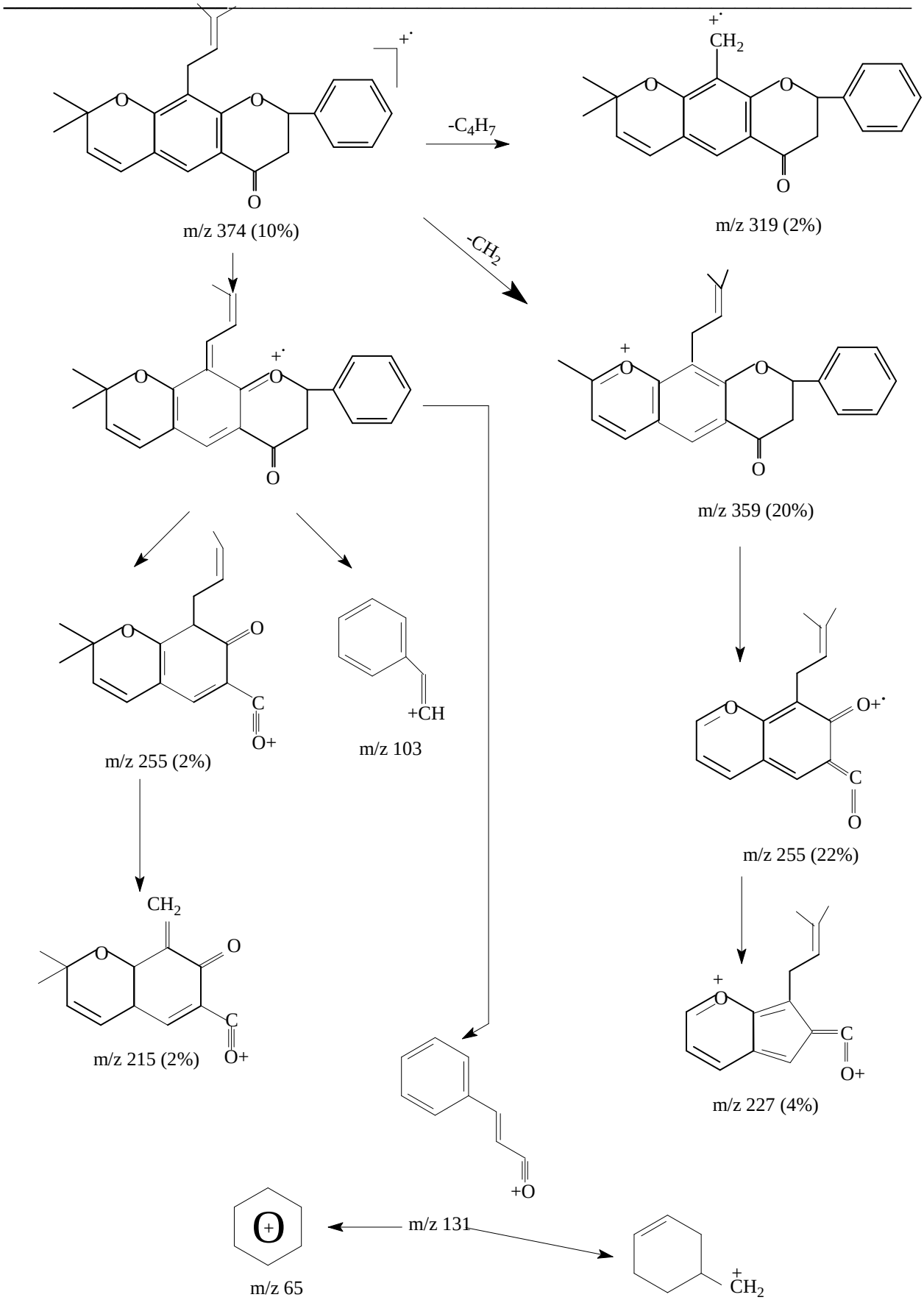
IR, υ^{KBr}_{max} cm^{-1}: 3520, 1650, 1630, 1602, 1575, 1512, 1450, 1060, 1035, 990, 835.

UV, λ_{max} nm: EtOH: 270, $AlCl_3$: 280, NaOAc: 277.

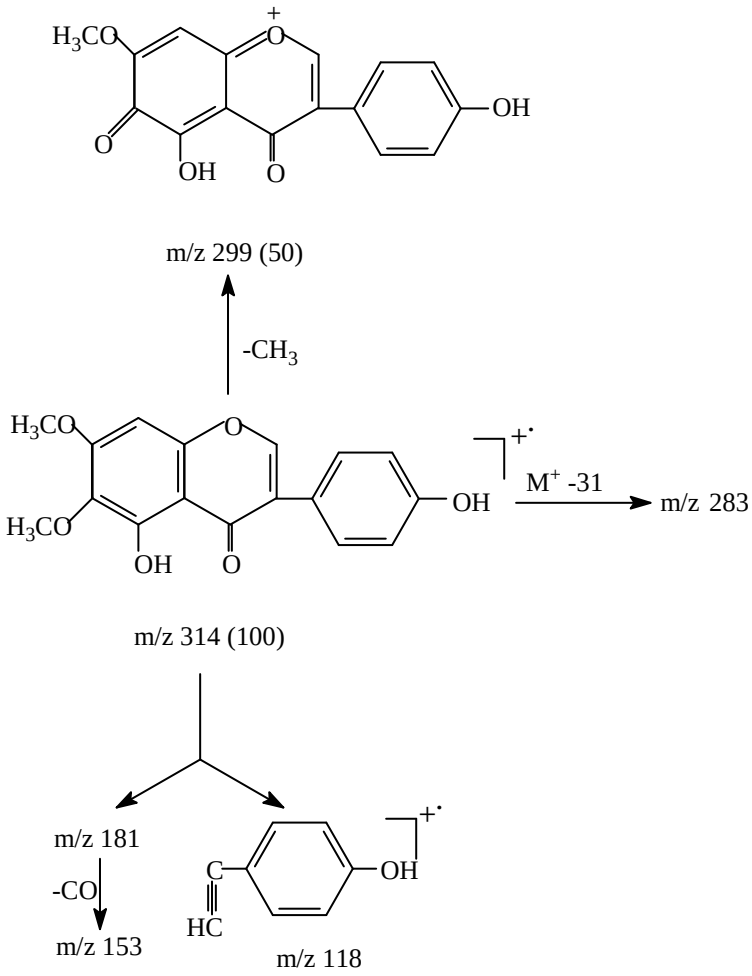
^{1}H-NMR (60MHz, $CDCl_3$ + DMSO-d_6) on δ scale: 3.8 (3H, s, -OCH_3), 3.9 (3H, s, -OCH_3), 6.5 (1H, s, 8-H), 6.9 (2H, d, J=10 Hz, 3',5'-H), 7.5 (2H, d, J=10 Hz, 2',6'–H), 7.9 (1H, s, 2–H).

Acetylation of La-4: La-4 (50 mg) was dissolved in pyridine (0.5 ml) and acetic anhydride (1 ml) was added to it. The mixture was allowed to stand for 24 hrs at room temperature. After 24 hours crushed ice was added to it and stirred vigorously. The Dirty white solid separated was crystallized from methanol in colourless needles, m.p. 162-63^{0}C. Analysed for $C_{21}H_{16}O_8$: Calcd.: C, 63.31; H, 4.52%, Found: C, 63.48; H, 4.59%.

Methyl ether: A mixture of **La-4** (150 mg) freshly distilled dimethyl sulphate (0.7 ml), anhydrous potassium carbonate (1 gm) and dry acetone (20 ml) was refluxed for 36 hours. The reaction mixture was filtered and the inorganic residue washed several times with hot acetone. The washings were combined and concentrated to a smaller volume. To the concentrate to water was added. The dirty white precipitate obtained, was washed with water and dried. On crystallization from ethylacetate colourless plates (130 mg) m.p. 181^{0}C were obtained. Analysed for $C_{19}H_{18}O_6$: Calcd.: C, 66.66; H, 5.26%, Found: C, 66.48; H, 5.29%.


-C4H7
m/z 374 (10%)
m/z 319 (2%)
-CH2
m/z 359 (20%)
m/z 255 (2%)
m/z 103
m/z 255 (22%)
m/z 215 (2%)
m/z 227 (4%)
m/z 131
m/z 65

(Scheme -I)



(Scheme-II)

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