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Epoxy Chromenes: The Therapeutic Agents from *Flemengia strobilfera*

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New epoxy chromenes; flemingin X, Y and Z have been isolated from the leaves of *Flemengia strobilifera*. They have been identified by chemical and spectroscopic methods.

INTRODUCTION

Flemengia strobilifera[1, 2] is commonly known as *Kusrunt*, belongs to sterculaceae family. The plant is reported to be useful in epilepsy and hysteria. In view of the signficant medicinal uses, the plant was phytochemically examined. The chloroform : acetone (1 : 1) extract of its leaves when worked up yielded three chromenes. They have been identified as flemingin X, Y and Z respectively.

RESULTS AND DISCUSSION

Compound (1) *i.e.*, flemingin-X was obtained as a resinous mass, m.p. 180–181°, $[\alpha]_D^{25}$ = +2.4° ($CHCl_3$). The UV absorption at 293 and 412 nm confirmed the chalcone structure. Positive Dimroth test[3] and a bathochromic shift of 40 nm on addition of $AlCl_3$ indicated the chelated OH group[4] in it. A band at 6.15 in the NMR spectrum indicated the ν(C═O), chelated to the OH group. The triacetate (2) showed UV absorption at 259 and 290 nm thereby confirming the chalcone skeleton. The NMR spectrum of (1) showed one chelated OH (sharp δ = 13.63), three phenolic OH (δ = 7.45, 7.91, 8.65) and an AB quartet with J = 15.5 Hz (DH═CH—*trans*). The strong down field shift of these two protons (δ = 7.83 and 8.20) provided evidence for the chalacone sesquence, Aryl—CH═CH—CO—Aryl. The aromatic part showed a singlet at δ7.45, and an ABX pattern of five lines. A triplet for the X-part of δ 7.28 and doublet for the AB (A = B = δ 6.85), with the same separation of 1.53 Hz partially overlapped by another signal, thereby confirming the sequence 1, 2,4 of the aromatic protons. The signal at 7.49 was for the proton of the another benzene ring, whereas the AB pattern of two doublets at δ 6.78 and δ 5.69 (J = 10 Hz) confirmed the chromene ring[5].

The tertiary methyl groups (δ 1.45, δ 1.55) and a two proton triplet at δ 5.14 (J = 1 Hz) indicated an isoprene chain.

Modified Kuhn-Roth oxidation of hexahydro derivative of (1) gave a volatile ketone, identified as 6-methyl hepta-2-one by GLC and TLC.

Chromic acid oxidation afforded 4,8-dimethyl-4-hydroxy-nonanoic acid lactone (3). These results confirmed the presence of 2-methyl-2-(4′-methyl pent-3′-ethyl) chromene ring with an asymmetric C-atom because of the optical activity of (1).

Ozonolysis of the triacetate (2) gave a carboxyl compound (4). It exhibited λ_{max} = 246, 295 nm, λ_{max} = 5.58 (—O—C—CH_3), and 5.90 (—CHO). The NMR spectrum in CCl_4 showed one-CHO (δ = 10.10), two acetyl (δ = 2.19 and 2.15) and three aromatic protons of ABC pattern with A = δ 7.12, B = δ 7.28, C = δ 7.55 (*ortho* to —CHO)), JAB = δ8.5 (*ortho*), J_{BC} = δ2.5 (*meta)* and J_{AC} = δ 0.6 (H_3, *para*). The compound was identified as 2-5-diacetoxy benzaldehyde, by comparing the UV and IR spectra with those of an authentic sample. Thus, the isolated compound (1) was indentified as flemingin-X.

Compound (5) was obtained as resinous mass, m.p. 148–150°C, $[\alpha]_D^{20}$ = –42°, showed UV absorption very similar to that of compound (1) but with a hypsochromic shift (λ_{max} = 295, 376 nm). Under stronger conditions gave triacetate (6). The NMR spectrum of (5) was very close to that of (1) except for the presence of three OH groups and the aromatic hydrogen of ring A: A = δ 6.95, B = δ 6.88, C = δ 7.24 and D = δ 7.81. Thereby confirming, the four protons of ring A were all *ortho* to each other, and also the presence of one OH group on ring A.

Ozonolysis of the triacetate (6) gave *ortho*-acetoxybenzldehyde, identified by mixed m.p. Thus, the identity of (5) was flemingin-Y.

Compound (7) was also obtained as resinous mass, m.p. 176–178°C, $[\alpha]_D^{20}$ = +6.7°, UV, max: 278, 285, and 376 nm.

The four phenolic hydroxyls lied at δ = 7.49, 9.15 (2H) and δ = 13.75 (chelated). The aromatic hydrogen on ring B appeared at δ = 7.34. The three aromatic protons on ring A appeared as AB_2 pattern with J_{AB} = 8.28 Hz, A = δ 6.95 and B = δ 6.51.

Ozonolysis yielded 2,6-diacetoxy-benzaldehyde, identified by Co Pc and TLC, thereby confirming the identity of (7) as flemingin—Z.

EXPERIMENTAL

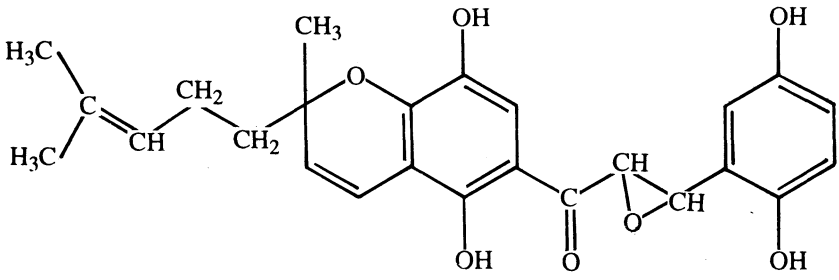
Isolation of flemingin X, Y and Z

The air dried, powdered leaves (5 kg) of *Flemengia strobilifera* were defatted with petroleum ether (40–60°C) in soxhlet extractor.

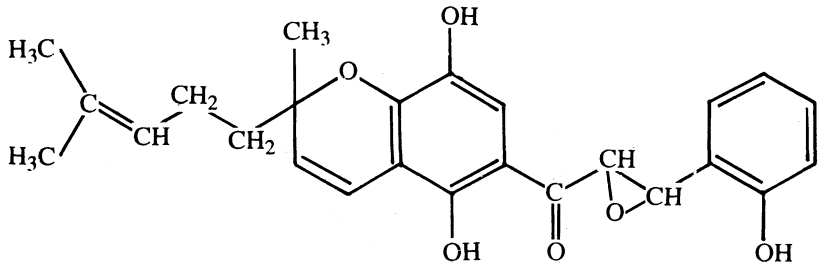
The defatted plant material (4 kg) was exhaustively extracted with chloroform : acetone (1:1), when a brown coloured extract was obtained the extract was concentrated to a viscous mass under reduced pressure.

The viscous mass on solidification after treatment with cold $CHCl_3$ to red resinous mass (40 g), column chromatographed on Si gel (hexane : ethylacetate, 4:1) gave compound (1), (5) and (7). (1) analyzed for $C_{25}H_{26}O_6$ (found C = 73.92, H = 6.36; calcd. C = 73.89, H = 6.40); M^+ = 422; m.p. 149–150°C $[\alpha]_D^{20}$ = –4.2 ($CHCl_3$); UVλ_{max}^{EtOH} nm; 295, 376.

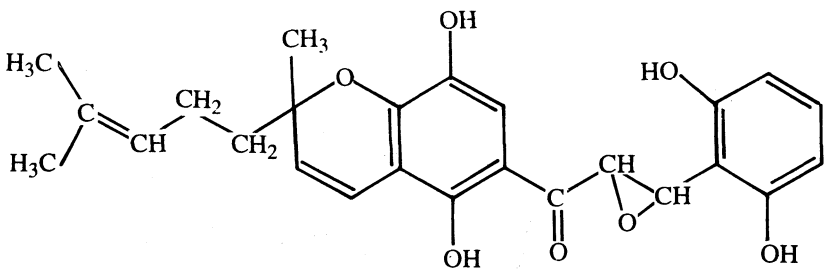
Acetylation of (1): 100 mg of (1) were refluxed for 1 h with Ac_2O (3 mL) and AcONa (50 mg) working of gave triacetate(2) as an oil; UV λ_{max}^{EtOH} = 229, 295 nm.



Flemingin-X



Flemingin-Y



Flemingin-Z

Ozonolysis of (2): A solution of 100 mg of (2) in 8 mL of $CH_3COOC_2H_5$ was cooled with dry acetone and flow of ozonised O_2 was bubbled through it for 10 min. Few drops of water added and the solvent evaporated, the residue extracted with ether. Chromatography of the extract with $CHCl_3$:ether (2:1) gave in the first fraction 2-acetone benzaldehyde, identified by TLC, GLC and IR comparison.

Compound (5): Analysed for $C_{25}H_{26}O_7$ (found C = 71.21, H = 6.28; calcd. C = 71.07, H = 6.20), $M^+ = 438$; m.p. = 176–178°C, UV λ_{max}^{EtOH} nm: 278, 285 and 376.

Flemingin Y tetraacetate: Analyzed for $C_{33}H_{34}O_{11}$ (found C = 66.99, H = 5.73; calcd. C = 67.11, H = 5.80%); M^+ = 6.06..

Ozonolysis of the tetraacetate: As described the ozonolysis of flemingin X gave 2,6-diacetoxy benzaldehyde, m.p. = 92–93°C, λ_{max}^{EtOH} nm = 247 and 295 nm.

Hexahydro flemingin Y: Flemingin Y (300 mg) in 100 mL dry MeOH were reduced with H_2 in presence of 60 mg of 5% Pd/C; 3 moles/mole were absorbed. Evaporation and chromatography with (hexane:AcOEt) (1:1) yielded 200 mg of white crystals, m.p. 145–146°C, analyzed for $C_{25}H_{32}O_7$ (found C = 70.21, H = 7.62; calcd. C = 70.07, H = 7.53%); M^+ = 444.

Flemingin Z (7): Analyzed for $C_{25}H_{26}O_7$ (found C = 71.23, H = 6.24; calcd. C = 71.07, H = 6.20%); M^+ = 358, m.p. 180–182°C.

Tetra acetate of (7): Analyzed for $C_{33}H_{34}O_{11}$ (found C = =68.00, H = 5.82; calcd. C = 67.11, H = 5.80%), M^+ = 556, m.p. 108–11°C.

Hexahydroflemingin Z: Flemingin Z (1.6 g) in 200 mL CH_3OH was hydrogenated with 86 mg. PtO_2 as the catalyst. Evaporation and chromatography with hexane AcOEt (4:1), gave 900 mg of the compound, m.p. 135°C; analysed for $C_{25}H_{32}O_7$ (found C = 70.67, H = 7.73; calcd. C = 70.07, H = 7.53%); M^+ = 444.

Ozonolysis of flemingin Z tetraacetate

It was carried out as in case of flemingin X.

Kuhn-roth oxidation of hydroflemingin Z-triacetate

Hexahydroflemingin-Z-triacetate (85.0 g) was treated with 50 mL of the oxidising solution according to Karrer schimid and distilled. The distillate was neutralized and extracted with ether.

It contains 2-methyl-heptanone as identified by TLC and GLC.

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