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PHYTOCHEMICAL INVESTIGATION OF THE FRUITS OF *ZANTHOXYLUM ARMATUM* DC.

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ABSTRACT

Zanthoxylum armatum DC. (family Rutaceae) is a thorny shrub or small tree found in south eathern Asia. Its fruits and seeds are used to treat arthritis, asthma, blood diseases, bronchitis, bruises, cancer, cholera, diabetes, depression, digestive impairment, dyspepsia, earache, fever, fibrositis, headache, heart diseases, microbial infections, piles, roundworms, skin diseases, swellings, toothache and worms. Our study was planned to isolate chemical constituents from a methanolic extract of the fruits of this plant and to characterize their structures on the basis spectral data analysis. Phytochemical investigation of the fruits of *Z. armatum* led to isolate two aromatic esters identified as 2, 8-dimethyl-non-4 (Z)-en-8-ol-2-olyl benzoate (**1**) and 2, 10-dimethyl-undec-6- (Z)-en-10-ol-2-olyl benzoate (**2**), two flavanols characterized as 7,8,4′-trimethoxy-3,5-dihydroxyflavanol (tambulin, **3**) and 3,5,8-trihydroxy-7, 4′-dimethoxyflavanol (**4**) and 3,4,5-trihydroxyphenoxy-3′,4′,5′-trihydroxybenzene (**5**). The structures of isolated chemical constituents were established on the basis of analysis of spectral data and chemical means.

KEYWORDS: *Zanthoxylum armatum*, fruits, phytoconstituents, isolation, structure elucidation.

INTRODUCTION

Zanthoxylum armatum DC., syn. *Zanthoxylum alatum* Roxb. (family Rutaceae), known as Timur, Tephal, Indian Prickly Ash, Nepal Pepper, Toothache tree, is found in the temperate Himalaya, Kashmir, south eastern Asia and south western China as a small, dioecious, spiny shrub, up to 3.5 m high, corky bark, stems and branches armed with prickles or straight spines, leaves with stipular spines at the base, leaflets gland-dotted, small whitish green yellow flowers in short branched lateral clusters, globular wrinkled aromatic capsules, shining black seeds, reddish globose fruits used as condiment and also pickled.[1-3]

The fruits are regarded as an anthelmintic, antiseptic, antispasmodic, carminative, deodorant, disinfectant, fish poison, fungistatic, insect and leech repellent, stomachic, aromatic tonic and mouth-freshener, used to treat cholera, cold, cough, abdominal pains, diarrhoea, dysentery, dyspepsia, fever, tonsillitis, limbs numbness, skin diseases and toothache.

Powdered seeds are aromatic, antibacterial, anthelmintic, carminative and eaten to relieve dyspepsia, stomach disorders, indigestion and cholera. The fruits and seeds are useful against dental complaints.[1-5]

The fruits and seeds of *Z. armatum* contained an essential oil,[6-9] amide[10], phenolic constituents, anthraquinones, aromatic acids, phytosterol[11], flavonoids, phenolic compounds[12-14], aromatic esters and fatty acids[15], 2α-methyl-2β-ethylene-3β-isopropyl-cyclohexan-1β, 3α-diol, linoleiyl-O-α-D-xylopyranoside, tambulin, prudomestin, obmuin and hexahydroxydiphenyl ether[14], aliphatic amides and chlorogenic acid.[16] Keeping in view the high reputation and wide application of the plant parts of *Zanthoxylum armatum* in many indigenous medicinal systems, it has been aimed to analyze the spectral data to establish structures of the phytoconstituents isolated from fruits of this plant collected from Chamoli region, Uttarakhand.

MATERIAL AND METHODS

The protocols of all methodologies (procedures, experimental designs and spectral data analysis) were adopted from the earlier published work.[11, 13]

General procedures

Melting points were determined on a Perfit melting point apparatus (Ambala, India) and are uncorrected. IR spectra were recorded using KBr pellets, with a Jasco FT/IR-5000 Spectrometer (FTS 135, Hongkong). UV spectra were measured with a Lambda Bio 20 Spectrophotometer (Perkin Elmer, Schwerzenbach,

Switzerland) in methanol. ^{1}H and ^{13}C NMR spectra were recorded using Bruker ARX- 400 NMR spectrometer (Rheinstetten, Germany), in $CDCl_3$ and with TMS as an internal standard. The chemical shifts were measured in δ values (ppm). Mass spectra were obtained using a JEOL-JMS-DX 303 spectrometer (Peabody, MA, USA). Column chromatography was performed on silica gel (Qualigens, Mumbai, India), 60–120 mesh. TLC plates were run on silica gel G (Qualigens). Spots were visualized by exposure to iodine vapours, UV radiation and by spraying with ceric sulphate solution.

Collection of plant material

The fruits of *Z. armatum* were collected from district Chamoli (Uttarakhand) and identified by Dr. M. P. Sharma, Professor and Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. A voucher specimen is deposited in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

Preparation of extract and isolation

The fruits of *Z. armatum* (1.5 kg) were dried at 45°C, coarsely powdered and extracted exhaustively with methanol in a Soxhlet apparatus. The methanolic extract was dried on a steam bath under reduced pressure to get dark brown mass (153 g, 10.2 % yields). The dried methanolic extract was defatted with petroleum ether.

The dried defatted methanolic extract was dissolved in minimum amount of methanol to attain the desired consistency. Silica gel for column chromatography (60-120 mesh) was added gradually with constant mixing to obtain a slurry. The slurry was dried in air and chromatographed over silica gel column (1.6 m x 16 mm x 2 mm) packed in chloroform. The column was eluted successively in increasing order of polarity in various combinations with chloroform and chloroform-methanol (99 : 1; 97 : 3; 19 : 1; 93 : 7; and 9 : 1; v/v). The fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized. The isolated compounds were recrystallized to get the following compounds:

2, 8-Dimethyl-non-4 (Z)-en-8-ol-2-olyl benzoate (1)

Elution of the column with chloroform afforded a pale yellow semisolid mass of **1**, UV λ_{max} (MeOH): 253, 262, 279 nm **(**log ε 3.8, 2.1, 5.3); IR υ_{max} (KBr): 3398, 2928, 2853, 1723, 1635, 1551, 1431, 1381, 1174, 1019, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.75 (1H, m, H-2′), 6.04 (1H, m, H-6′), 5.97 (1H, m, H-4′), 5.92 (1H, m, H-3′), 5.88 (1H, m, H-5′), 5.57 (1H, m, $w_{1/2}$ = 8.5 Hz, H-4), 5.56 (1H, m, $w_{1/2}$ = 8.6 Hz, H-5), 3.21 (2H, m, H_2-3), 2.21 (2H, m, H_2-6), 1.64 (2H, d, J = 7.3 Hz, H_2-7), 1.29 (12H, br s, Me- 1), Me-9, Me-10, Me-11); ^{13}C NMR ($CDCl_3$): δ 18.51 (C-1), 71.83 (C-2), 33.23 (C-3), 125.25 (C-4), 130.09 (C-5), 32.73 (C-6), 51.31 (C-7), 71.75 (C-8), 27.31 (C-9), 18.48 (C-10), 27.38 (C-11), 145.31 (C-1′), 133.02 (C-2′), 133.26 (C-3′), 131.57 (C-4′), 133.29 (C-5′), 132.91 (C-6′), 169.32 (C-70); ESIMS *m/z* (rel. int.): 291 $[M+H]^+$ ($C_{18}H_{27}O_3$) (10.7), 203 (8.2), 177 (10.6).

2,10-Dimethyl-undec-6-(Z)-en-10-ol-2-olyl benzoate (2)

Further elution of the column with chloroform eluents gave pale yellow semisolid mass of **2**, UV λ_{max} (MeOH): 269 nm **(**log ε 5.1); IR υ_{max} (KBr): 3408, 2968, 2917, 1722, 1638, 1557, 1427, 1374, 1262, 1161, 989, 902 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.81 (1H, m, H-2′), 6.11 (1H, m, H-6′), 6.05 (1H, m, H-4′), 5.87 (1H, m, H-3′), 5.79 (1H, m, H-5′), 5.68 (1H, m, $w_{1/2}$ = 7.6 Hz, H-7), 5.59 (1H, m, $w_{1/2}$ = 8.6 Hz, H-6), 3.27 (2H, m, H_2-5), 2.51 (2H, m, H_2-3), 2.32 (2H, m, H_2-4), 2.25 (2H, m, H_2-5), 1.75 (2H, d, J = 7.4 Hz, H_2-9), 1.21 (12H, br s, Me- 1, Me-11, Me-12, Me-13); ^{13}C NMR ($CDCl_3$): δ 18.29 (C-1), 70.67 (C-2), 32.12 (C-3), 31.91 (C-4), 31.78 (C-5), 123.54 (C-6), 129. 41 (C-7), 50.19 (C-8), 31.41 (C-9), 70.85 (C-10), 27.01 (C11), 26.46 (C-12), 18.21 (C-13), 144.29 (C-1′), 132.08 (C-2′), 131.48 (C-3′), 130.12 (C-4′), 131.43 (C-5′), 131.57 (C-6′), 167.36 (C-7′); ESIMS *m/z* (rel. int.): 319 $[M+H]^+$ ($C_{20}H_{31}O_3$) (69.8), 231 (12.7), 205 (9.1), 163 (14.3), 155 (21.6).

Tambulin (3)

Elution of the column with chloroform – methanol (49:1) furnished pale yellow crystals of **3**, recrystallized from acetone, 135 mg, m. p. 203 - 205 ° C, UV λmax (MeOH) : 325, 271 nm (log ε 6.9, 3.4); IR υmax (KBr): 3327, 2924, 2853, 1683, 1642, 1555, 1407, 1364, 1317, 1097, 805 cm^{-1}; ^{1}H-NMR ($CDCl_3$) : δ 11.58 (1H, s, C-5 OH), 7.13 (2H, d, = 9.0 Hz, H-3′/H-5′), 8.27 (2H, d = 9.0 Hz, H-2′/H-6′), 6.55 (1H, s, C-3 OH), 6.51 (1H, s, H-6), 3.86 (3H, s, C-4′ OMe), 3.90 (3H, s, C-7 OMe), 3.98 (3H, s, C-8 OMe); ^{13}C NMR ($CDCl_3$) : δ 146.3 (C-2), 138.2 (C-3), 162.4 (C-4), 159.71 (C-5), 98.8 (C-6), 159.1 (C-7), 130.8 (C-8), 145.1 (C-9), 113.9 (C-10), 125.2 (C-1′), 113.8 (C-2′), 128.6 (C-3′), 151.3 (C-4′), 114.3 (C-5′), 127.0 (C-6′), 55.3 (OMe), 53.6 (OMe), 52.8 (OMe); ESIMS *m/z* (rel. int.) 344 $[M]^+$ ($C_{18}H_{16}O_7$) (6.3).

3,5,8-Trihydroxy-7, 4′-dimethoxyflavone (4)

Elution of the column with chloroform – methanol (19:1) afforded pale yellow crystals of **4**, recrystallized from acetone, 135 mg, m. p. 203 - 205 ° C, UVλmax (MeOH) : 321, 278 nm (log ε 7.1, 3.2); IR υmax (KBr): 3341, 2928, 2849, 1687, 1645, 1549, 1411, 1368, 1321, 1089, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.27 (1H, d, *J* = 9.0 Hz, H-2′), 8.24 (1H, d, *J* = 9.0 Hz, H-6′), 7.13 (1H, d, *J* = 9.0 Hz, H-3′), 7.10 (1H, d, J = 9.0 Hz, H-5′), 6.30 (1H, s, H-6), 3.98 (3H, brs, OMe), 3.88 (3H, brs, OMe); ^{13}C NMR ($CDCl_3$): δ 146.10 (C-2), 136.48 (C-3), 176.38 (C-4), 157.09 (C-5), 98.60 (C-6), 161.62 (C-7), 128.45 (C-8), 156.71 (C-9), 103.67 (C-10), 124.02 (C-1′), 114.03 (C-2′), 114.46 (C-3′), 147.28 (C-4′), 114.46 (C-5′), 98.71 (C-6′), 55.5 (OMe), 53.48 (OMe); ESI MS *m/z* 330 $[M]^+$ ($C_{17}H_{14}O_7$) (6.2).

3,4,5-Trihydroxyphenoxy-3′,4′,5′-trihydroxybenzene (5)

Further elution of the column with chloroform – methanol (19:1) produced grey crystals of **5**, recrystallized from acetone, 123.0 mg, m. p. 166 – 168 ° C, R_f 0.32 (chloroform – methanol, 9.5 – 0.5, v/v), UVλmax (MeOH) : 226, 293 nm (log ε 4.7, 2.8); IR υmax (KBr): 3397, 3288, 2925, 2843, 1641, 1543, 1386, 1221, 1068 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.76 (4H, br s, H-2, H-6, H-2′, H-6′); ^{13}C NMR ($CDCl_3$): δ 150.17 (C-1, C-1′), 117.21 (C-2, C-2′), 116.91 (C-6, C-6′), 148.72 (C-3, C-5), 150.21 (C-4), 149.06 (C-3′, C-5′), 150.14 (C-4′); ESI MS *m/z* 266 $[M]^+$ ($C_{12}H_{10}O_7$) (1.5).

RESULT AND DISCUSSION

Compound **1** was obtained as a yellow semi-solid mass from the chloroform eluents. Its UV absorption maxima at 262 and 279 nm indicated the presence of aromatic nature of the molecule. Its IR spectrum displayed absorption bands for a hydroxyl group (3398 cm^{-1}), ester function (1723 cm^{-1}), aromatic ring (1551, 1019 cm^{-1}), and unsaturation (1635 cm^{-1}). Its molecular ion peak was determined at *m/z* 291 $[M+H]^+$ on the basis of mass and ^{13}C NMR spectra corresponding to the molecular formula of an aromatic ester with aliphatic chain $C_{18}H_{27}O_3$. The ion peaks arising at *m/z* 177 [C_3 - C_4 fission, $C_{11}H_{13}O_2]^+$ and 203 [C_5 – C_6 fission, $C_{13}H_{15}O_2]^+$ suggested the presence of the vinylic linkage at C_4 carbon.

The ^1H NMR spectrum of compound **1** showed deshielded five one-proton mutiplets between δ 6.75 - 5.88 assigned to aromatic protons H-2′, H-6′, H-4′, H-3′ and H-5′ protons. Two one-proton multiplets at δ 5.57 ($w_{1/2}$ = 8.5 Hz) and 5.56 ($w_{1/2}$ = 8.6 Hz) were ascribed to cis-oriented vinylic H-4 and H-5 protons, respectively. Two two-proton multiplets at δ 3.21 and 2.21 and a two-proton doublet at δ 1.64 (J = 7.3 Hz) were attributed to methylene H_2-3, H_2-6 and H_2-7 protons, respectively. A broad singlet at δ 1.29 (12 H) was associated with tertiary C-1, C-9, C-10 and C-11 methyl protons. The ^{13}C NMR spectrum of **1** exhibited a signal for ester carbon at δ 169.32 (C-7′), vinylic carbons appeared at δ 125.25 (C-4) and 130.09 (C-5), six aromatic carbons between δ 145.31- 132.61, methylene carbons at δ 33.23 (C-3), 32.73 (C-6) and 51.31 (C-7), oxy-substituted carbons at δ 71.83 (C-2) and 71.75 (C-8) and methyl carbons at δ 18.51 (C-1), 27.31 (C-9), 18.48 (C-10) and 27.38 (C-11). On the basis of these spectral data studies, the structure of **1** has been established as 2, 8-dimethyl-non-4 (Z)-en-8-ol-2-olyl benzoate, a new compound and reported first time in nature (Fig. 1).

Compound **2** was obtained as a yellow semi-solid mass from the chloroform eluents. The UV absorption maxima at 269 nm due to the presence of aromatic nature of the molecule. Its IR spectrum exhibited absorption bands for a hydroxyl group (3408 cm^{-1}), ester function (1722 cm^{-1}), aromatic ring (1557, 989 cm^{-1}), and unsaturation (1638 cm^{-1}). Its molecular ion peak was established at *m/z* 319 $[M+H]^+$ on the basis of mass and ^{13}C NMR spectra corresponding to the molecular formula of an aromatic ester with aliphatic chain $C_{20}H_{30}O_3$. The ion peaks formed at *m/z* 163 [C_2 – C_3 fission, $C_{10}H_{11}O_2]^+$ and 155 $[M - 163]^+$ suggested the presence of benzoate unit at one of end of the molecule. The ion fragments generated at *m/z* 205 [C_5 – C_6 fission, $C_{13}H_{17}O_2]^+$ and 231 [C_7 – C_8 fission, $C_{15}H_{19}O_2]^+$ supported the existence of the vinylic linkage at C_6 carbon.

The ^1H NMR spectrum of compound **2** displaced deshielded five one-proton mutiplets between δ 6.81 - 5.79 in the downfield region ascribed to aromatic protons H-2′, H-6′, H-4′, H-3′ and H-5′ protons. Two one-proton multiplets at δ 5.68 ($w_{1/2}$ = 7.6 Hz) and 5.59 ($w_{1/2}$ = 8.6 Hz) were accounted to cis-oriented vinylic H-7 and H-6 protons, respectively. Four two-proton multiplets at δ 3.27, 2.51, 2.32 and 2.25 and a two-proton doublet at δ 1.75 (J = 7.4 Hz) were attributed to methylene H_2-5 H_2-3, H_2-4, H_2-5 and H_2-9 protons, respectively. A broad singlet at δ 1.21 (12 H) was associated with tertiary C-1, C-11, C-12 and C-13 methyl protons. The ^{13}C NMR spectrum of **2** showed a signal for ester carbon at δ 167.36 (C-7′), vinylic carbons at δ 123.54 (C-6) and 129. 41 (C-7), six aromatic carbons between δ 144.29 – 130.12, methylene carbons at δ 32.12 (C-3), 31.91 (C-4), 31.78 (C-5), 50.19 (C-8), and 31.41 (C-9), oxy-substituted carbons at δ 70.67 (C-2) and 70.85 (C-10) and methyl carbons at δ 18.29 (C-1), 27.01 (C-11), 26.46 (C-12) and 18.21 (C-13). On the basis of these evidences of spectroscopic studies, the structure of **2** was elucidated as 2, 10-dimethyl-undec-6- (Z)-en-10-ol-2-olyl benzoate, a new aromatic ester reported the first time in nature (Fig. 1).

Compound **3** was obtained as a pale yellow crystalline mass from chloroform – methanol (49:1) eluents. It reacted positively to Shinoda and ferric chloride tests and showed UV absorption maxima at 271 and 325 nm distinctive for flavanols.[17,18] Its IR spectrum displayed characteristic absorption bands for hydroxyl groups (3327 cm^{-1}), carbonyl group (1683 cm^{-1}), and aromatic ring (1555, 1097 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, its molecular ion peak was established at *m/z* 344 $[M]^+$ consistent with the molecular formula of a flavanol, $C_{18}H_{16}O_7$.

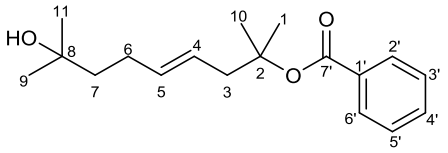
The ^1H NMR spectrum of **3** displayed a one-proton singlet at δ 6.51 assigned to H-6 of the flavanol. Two two-proton doublets at δ 7.13 (J = 9.0 Hz) and 8.27 (J = 9.0 Hz) were ascribed to ortho-coupled H-3′, H-5′ and H-2′, H-6′, respectively. Three three-proton broad signals at δ 3.86, 3.90 and 3.98 were ascribed to methoxy protons linked correspondingly to C-4′, C-7 and C-8 carbons. Two one-proton D_2O exchangeable signals at δ 11.58 and 6.55 were attributed to hydroxyl protons. The ^{13}C NMR spectrum of **3** exhibited signals for carbonyl carbon at δ 162.4 (C-4), flavanol carbons between δ 159.7 – 98.8, and methoxy carbons at δ 55.3, 53.6 and 52.8. The ^1H and ^{13}C NMR values of **3** were compared to the related

flavanol type flavonoids.[18] On the basis of foregoing discussion the structure of **3** has been formulated as 7,8,4′-trimethoxy-3,5-dihydroxyflavanol (tambulin) (Fig. 1).

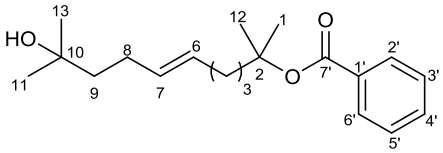
Compound **4** was obtained as a pale yellow crystalline mass from chloroform- methanol (19:1) eluents. It responded to Shinoda and ferric chloride tests positively and showed UV absorption maxima at 278 and 321 nm distinctive for flavanols.[16,17] Its IR spectrum exhibited characteristic absorption bands for hydroxyl groups (3341 cm^{-1}), carbonyl group (1687 cm^{-1}), and aromatic ring (1549, 1089 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, its molecular ion peak was established at *m/z* 330 $[M]^+$ corresponding to the molecular formula of a flavanol, $C_{17}H_{14}O_7$.

The ^1H NMR spectrum of **4** displayed a one-proton singlet at δ 6.30 assigned to H-6 of the flavanol. Four one -proton doublets at δ 8.27 (J = 9.0 Hz), 8.24 (J = 9.0 Hz), 7.13 (J = 9.0 Hz), and 7.10 (J = 9.0 Hz), were ascribed to ortho-coupled H-2′, H-6′, H-3′, and H-5′ protons, respectively. Two three-proton broad signals at δ 3.98 and 3.88 were attributed to methoxy protons linked correspondingly to C-4′ and C-7 carbons. The ^{13}C NMR spectrum of **4** exhibited signals for carbonyl carbon at δ 176.38 (C-4), flavanol carbons between δ 161.62 – 98.60, and methoxy carbons at δ 55.5 and 53.48. The ^1H and ^{13}C NMR values of **4** were compared with the related flavanols.[18] On the basis of foregoing discussion the structure of **4** has been established as 3,5,8-trihydroxy-7, 4′-dimethoxyflavanol (Fig. 1).

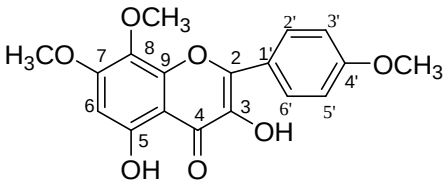
Compound **5** was obtained as a grey crystalline mass from chloroform methanol (19 : 1) eluents. It responded positively to ferric chloride tests and showed UV absorption maxima at 293 nm indicating phenolic nature of the compound. Its IR spectrum exhibited absorption bands characteristic for hydroxyl groups (3397, 3288 cm^{-1}), and aromatic ring (1641, 1543, 1068 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, its molecular ion peak was established at *m/z* 266 consistent with the molecular formula of a hexahydroxydiphenyl ether, $C_{12}H_{10}O_7$. The ^1H NMR spectrum of **5** showed a four -proton signal δ 6.76 assigned to aromatic H-2, H-6, H-2′, and H-6′ protons. The ^{13}C NMR spectrum of **5** exhibited signals for phenolic carbons at δ 150.17 (C-1, C-1′), 148.72 (C-3, C-5), 150.21 (C-4), 149.06 (C-3′, C-5′) and 150.14 (C-4′) and other aromatic carbons at δ 117.21 (C-2, C-2′) and 116.91 (C-6, C-6′). On the basis of these spectral data analysis, the structure of **5** has been determined as 3,4,5-trihydroxyphenoxy-3′,4′,5′-trihydroxybenzene (Fig. 1).



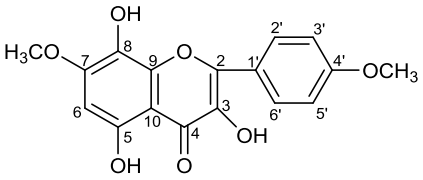
2,8-Dimethyl non-4(*Z*)-en-8-ol-2-olyl benzoate **(1)**



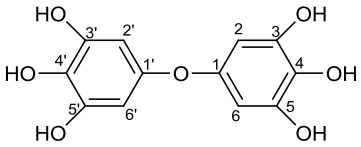
2,10-Dimethyl undec-6(*Z*)-en-10-ol-2-olyl benzoate **(2)**



Tambulin (**3**)



3,5,8-Trihydroxy-7,4′-dimethoxy flavone **(4)**



3,4,5-Trihydroxyphenoxy-3′,4′,5′-trihydroxybenzene **(5)**

Fig. 1: Structural formulae of the chemical constituents 1 to 5 isolated from the fruits of *Zanthoxylum armatum* DC.

CONCLUSION

Phytochemical investigation of the fruits of *Z. armatum* led to isolate two aromatic esters identified as 2, 8-dimethyl-non-4 (Z)-en-8-ol-2-olyl benzoate (**1**) and 2, 10-dimethyl-undec-6- (Z)-en-10-ol-2-olyl benzoate (**2**), two flavanols characterized as 7,8,4′-trimethoxy-3,5-dihydroxyflavanol (tambulin, **3**) and 3,5,8-trihydroxy-7, 4′-dimethoxyflavanol (**4**) and 3,4,5-trihydroxyphenoxy-3′,4′,5′-trihydroxybenzene (**5**). This work has enhanced understanding about the chemical constituents of the undertaken plants. Further research is recommended to screen bioactivities of the isolated phytoconstituents with a view for supplementing conventional drug development especially in developing countries.

ACKNOWLEDGEMENT

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