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Chemical constituents of the heartwood and bark of *Homonoia riparia*

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Abstract : Heartwood and stem bark extracts of *Homonoia riparia* Lour (Euphorbiaceae) were chemically examined which contained sterols, fatty acid, triterpenoids and their derivatives. The structural elucidations of the compounds were accomplished by spectral analysis. The presence of biologically important triterpene acid 3-acetyl aleuritolic acid has been reported for the first time from this Indian medicinal plant *Homonoia riparia.*

Key words: *H. riparia*, triterpenes, 3-acetyl aleuritolic acid.

INTRODUCTION

Homonoia riparia of Euphorbiaceae (Vernacular name: Adavi ganneru, Taniki), is a small genus of shrubs and small trees distributed from India to Guinea (Gamble, 1921), commonly found along river beds mixed with rocky boulders (Seshagiri Rao and Sreeramulu, 1986). Different parts of this plant are used for various ailments. The powdered root is laxative, diuretic and emetic; decotion of the root given for piles, stones in the bladder, chest pain, gonorrhea and syphilis. Powdered leaves and fruits are applied as poultice for skin diseases. In the Philippines, the mash obtained by chewing leaves is rubbed on wounds caused by scorpion fish (The Wealth of India, 1959; Ambasta, 1986). In earlier studies taraxerone, gallic acid and quercetin glycoside were reported from the leaves of *H. riparia* (Parveen et. al., 1988). Considering the above medicinal uses, the heartwood and bark extracts were chemically examined for their constituents and details reported in this paper.

MATERIALS AND METHODS

Experimental Procedures: The ^{1}H and ^{13}C NMR recorded in $CDCl_3$, d^6 –DMSO on Varian 400, 500, and Jeol JNM90 instruments, chemical shifts are reported in ppm relative to the internal standard TMS. The number of protons attached for 13C signals was determined by using APT pulse sequence. EI mass and FAB mass spectral measurements were recorded on Finnigan MAT 95 high-resolution double focusing (EB) mass spectrometer with Tandem Ion Trap.

Plant Material: *H. riparia* plant was collected from Masariguda Village, Palakonda forest range, Srikakulam District, Andhra Pradesh, India and voucher specimen deposited in the Department of Organic Chemistry, Andhra University under the accession code HR - PAR.

The stem bark material was carefully removed, shade dried separately and pulverized.

Extraction and Isolation: The powdered heartwood (1.8 kg) was extracted with methanol (10L) using soxhelet extraction apparatus and concentrated under reduced pressure to obtain red gummy residue (6.5gm). The residue was chromatographed over silica gel, eluted successively with n-hexane: ethyl acetate mixture by increasing polarity with 92 fractions collected (500ml each). Fractions 12-24 gave mixture of **1** (125mg) and **2** (100mg), which were separated by repeated chromatography and recrystallised from chloroform and methanol. Fractions 34-42 yielded a waxy solid **3** (45mg) and 64-71 gave colourless solid **4** (25mg). Fractions 81-86 yielded a brown solid, which was crystallised from ethanol, gave **5** (120mg).

The bark powder was successively extracted with n-hexane, chloroform, and methanol (5L each) at elevated temperatures. The solvent was removed in vacuo to leave the reddish brown extract. The n-hexane and chloroform extracts showing identical spots on T.L.C. were combined (2.8gm) and column chromatographed over silica gel, eluted with n-hexane: ethyl acetate mixture (44 fractions, 250ml each). Fractions 7-14, 18-28 and 34-41 yielded colourless solids **6, 7, 8** respectively, which were purified by repeated chromatography and crystallised from chloroform and methanol furnished **6** (125mg), **7** (35mg) and **8** (85mg). By

using a similar procedure the methanol extract yielded the compounds **1, 2, 5** and **7.**

Compound **(1):** β-sitosterol. Crystallised from chloroform-methanol as colourless needles. m.p. 135-136°C; $C_{29}H_{50}O$; ^1H NMR (400 MHz, $CDCl_3$): δ 0.68 (3H, s, 18-Me), 0.81 (6H, d, J = 7 Hz, 26,27-Me), 0.84 (3H, t, 29-Me), 0.89 (3H, d, J =6.3 Hz, 21-Me), 0.99 (3H, s, 19-Me), 3.21 (1H,m, 3α-H), 5.21 (1H, m, 6-H); ^{13}C NMR (100.20 MHz, $CDCl_3$): δ 37.3 (C-1), 31.8 (C-2), 71.9 (C-3), 42.4 (C-4), 140.9 (C-5), 121.8 (C-6), 32.0 (C-7), 32.0 (C-8), 50.3 (C-9), 36.6 (C-10), 21.1 (C-11), 39.9 (C-12), 42.4 (C-13), 56.8 (C-14), 24.3 (C-15), 28.2 (C-16), 56.2 (C-17), 11.9 (C-18), 19.4 (C-19), 36.4 (C-20), 19.1 (C-21), 34.0(C-22), 29.3 (C-23), 50.3 (C-24), 26.2 (C-25), 18.8 (C-26), 19.8 (C-27), 23.1 (C-28), 11.9(C-29).

Compound **(2):** Stigmasterol. Crystallised from chloroform-methanol as needles. m.p. 168-170°C, $C_{29}H_{48}O$; ^1H NMR (400 MHz, $CDCl_3$): δ 0.80, 0.85, 0.95, 1.02, 1.05, 1.20 (18H, 6xMe), 3.55 (1H, br, 3α-H), 5.15 (2H, m, 22, 23-H), 5.31 (1H, m, 6-H); ^{13}C NMR (100.20 MHz, $CDCl_3$): δ 37.4 (C-1), 31.7 (C-2), 71.8 (C-3), 42.4 (C-4), 140.9 (C-5), 121.7 (C-6), 31.9 (C-7), 31.9 (C-8), 50.3 (C-9), 38.6 (C-10), 21.1 (C-11), 39.8 (C-12), 42.4 (C-13), 57.0 (C-14), 24.4 (C-15), 28.9 (C-16), 56.0 (C-17), 12.2 (C-18), 19.4 (C-19), 40.5 (C-20), 21.1 (C-21), 138.4 (C-22), 129.4 (C-23), 51.3 (C-24), 31.9 (C-25), 19.0 (C-26), 21.1 (C-27), 25.4 (C-28), 12.0 (C-29).

Compound **(3):** 5-(E)-eicosenoic acid. (Low melting solid). Crystallised from n-hexane as waxy solid m.p. 56-57°C; $C_{20}H_{38}O_2$; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85 (3H, t, CH_3), 1.20-1.30 (24H, s, CH_2 x 12), 1.95-2.06 (4H, m, allylic CH_2), 2.30 (2H, s, CH_2COOH), 5.30 (2H, m, vinylic CH); ^{13}C NMR (22.50 MHz, $CDCl_3$): δ 179.63 (C-1), 34.01 (C-2), 24.70 (C-3), 31.92 (C-4), 130.02 (C-5), 129.70 (C-6), 27.20 (C-7), 29.06-29.65 (C-8 to C-18), 22.67 (C-19), 14.05 (C-20).

Compound **(4):** Gallic acid. Crystallised from methanol as colourless needles. m.p. 238-242°C; $C_7H_6O_5$; ^1H NMR (90 MHz, $CDCl_3$ + d⁶-DMSO): δ 7.11 (2H, s), 8.1 (3H, s), 12.18 (1H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$ + d⁶-DMSO): δ 108.10 (C-1), 120.45 (C-2, C-6), 137.12 (C-3, C-5), 145.4 (C-4), 168.32 (-OCO).

Compound **(5):** β-Sitosterol-3-O-β-D-glucoside. Crystallised from ethanol as crystalline solid. m.p. 274-276°C; $C_{35}H_{60}O_6$; I.R (KBr) ν^{max}: 3370, 2930, 2860, 1655, 1640 and 810 cm^{-1};

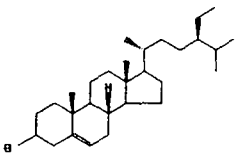
^1H NMR (400 MHz, d⁶-DMSO): δ 0.68 (3H, s, 18-Me), 0.79 (6H, d, J = 7.0 Hz, 26, 27-Me), 0.82 (3H, d, J = 6.3 Hz, 21-Me), 0.92 (3H, t, J = 7 Hz, 29-Me), 0.98 (3H, s, 19-Me), 3.46 (1H, m, 3α-H), 3.64-5.08 (sugar protons), 5.32 (1H, m, 6-H); ^{13}C NMR (125.70 MHz, d⁶-DMSO): δ 37.3 (C-1), 29.6 (C-2), 77.2 (C-3), 39.4 (C-4), 140.1 (C-5), 121.7 (C-6), 31.8 (C-7), 31.8 (C-8), 50.1 (C-9), 36.5 (C-10), 20.6 (C-11), 39.1 (C-12), 42.1 (C-13), 56.6 (C-14), 24.4 (C-15), 27.9 (C-16), 55.9 (C-17), 11.8 (C-18), 19.2 (C-19), 36.0 (C-20), 18.6 (C-21), 33.9 (C-22), 26.6 (C-23), 45.7 (C-24), 28.9 (C-25), 18.9 (C-26), 19.7 (C-27), 22.8 (C-28), 11.8 (C-29), 101.0 (C-1'), 73.8 (C-2'), 76.9 (C-3'), 70.3 (C-4'), 76.5 (C-5'), 61.2 (C-6'); E.I. Mass m/z (%): 576.5 (5) $[M^+]$, 414.25 (25) $[M-163+H]^+$, 399 (2) $[M-163+H-CH_3]^+$, 398.0 (5) $[M-163-CH_3]^+$, 397 (19) [M-179], 396.4 (84) [M-180 (Glucose)]⁺, 382.4 (16) $[M-179-CH_3]^+$, 161.0 (10) $[C_6H_{11}O_6 - H^2O]^+$.

Compound **(6):** Taraxerone. Crystallised from methanol as colourless plates. m.p. 242-244°C.; $C_{30}H_{48}O$; ^1H NMR (400 MHz, $CDCl_3$): δ 0.81 (3H, s, 28-Me), 0.88 (6H, s, 24, 29-Me),0.94 (3H, s, 30-Me), 0.98 (3H, s, 23-Me), 1.05 (6H, s, 26, 27-Me), 1.08 (3H, s, 25-Me), 2.52 (2H, m, H-2), 5.56 (1H, dd, J = 8.4 and 4 Hz,15-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.34 (C-1), 34.14 (C-2), 217.52 (C-3), 47.57 (C-4), 55.57 (C-5), 19.96 (C-6), 35.77 (C-7), 38.86 (C-8), 48.69 (C-9), 37.53 (C-10), 17.44 (C-11), 29.93 (C-12), 37.73 (C-13), 157.56 (C-14), 117.88 (C-15), 33.07 (C-16), 40.62 (C-17), 47.79 (C-18), 40.62 (C-19), 28.79 (C-20), 33.56 (C-21), 28.79 (C-22), 26.09 (C-23), 21.48 (C-24), 14.62 (C-25), 29.86 (C-26), 25.58 (C-27), 29.93 (C-28), 33.56 (C-29), 21.35 (C-30); E.I. Mass m/z (%):424.4 (18) $[M^+]$, 409.4 (10), 300.3 (25), 204 (100), 189.2 (22), 124.0 (16).

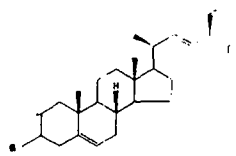
Compound **(7):** Taraxerol. Crystallised from chloroform-methanol as crystalline solid. m.p. 279-280°C; $C_{30}H_{50}O$; ^1H NMR (500 MHz, $CDCl_3$): δ 0.81 (3H, s, 24-Me), 0.84 (3H, s, 28-Me), 0.92 (6H, s, 25, 29-Me), 0.95 (3H, s, 30-Me), 0.98 (3H, s, 23-Me), 1.07 (6H, s, 26, 27-Me), 3.18 (1H, m, H-3), 5.44 (1H, dd, J = 8.1 and 4.0 Hz, 15-H); ^{13}C NMR (125.70 MHz, $CDCl_3$): δ 37.97 (C-1), 27.11 (C-2), 79.07 (C-3), 38.96 (C-4), 55.49 (C-5), 18.77 (C-6), 35.07 (C-7), 38.96 (C-8), 48.70 (C-9), 37.97 (C-10), 17.49 (C-11), 35.78 (C-12), 38.74 (C-13), 158.05 (C-14), 116.85 (C-15), 36.65 (C-16), 37.70 (C-17), 49.25 (C-18), 41.29 (C-19), 29.36 (C-20), 33.67 (C-21), 33.07 (C-22), 27.98 (C-23), 15.45 (C-24), 15.45 (C-25), 29.91 (C-26), 25.89 (C-27), 29.81 (C-28), 33.34 (C-29), 21.30 (C-30); EIMS m/z (%): 426.4 (5) $[M^+]$, 411 (11), 393 (9), 302 (36), 287 (35), 269 (27), 204 (100), 189 (38).

Compound **(8):** 3-Acetyl aleuritolic acid. Crystallised from chloroform-methanol as needles. m.p. 304-306°C; $[\alpha]_D^{25}$ +23.1 (0.6, $CHCl_3$); $C_{32}H_{50}O_4$; I.R ($CHCl_3$) ν^{max}: 3500, 1733, 1088 and 832 cm^{-1}; ^1H NMR (400 MHz,

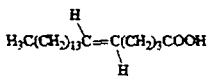
$CDCl_3$) and ^{13}C NMR (125.7 MHz, $CDCl_3$) See Table-1; EIMS m/z (%): 498.4 (2) [M^+], 344.3 (6), 329 (6), 248.1 (31), 234.1 (100), 189.2 (81) ; FAB mass M + Na^+ - 521.2 (16), 2M + Na^+ -1019.2 (100), 3M + Na^+ - 1518.1 (22).



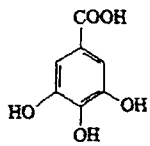
β-sitosterol (1)



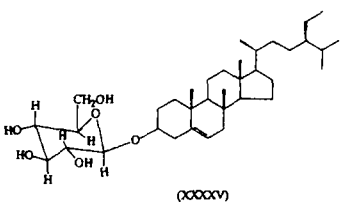
Stigmasterol (2)



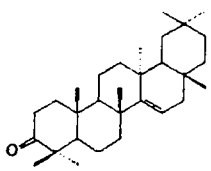
5(E)- eicosanoic acid (3)



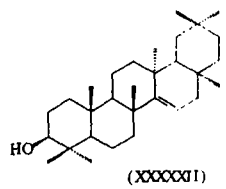
Gallic acid (4)



β-Sitosterol-3-O-β-D-glucoside (5)



Taraxerone (6)



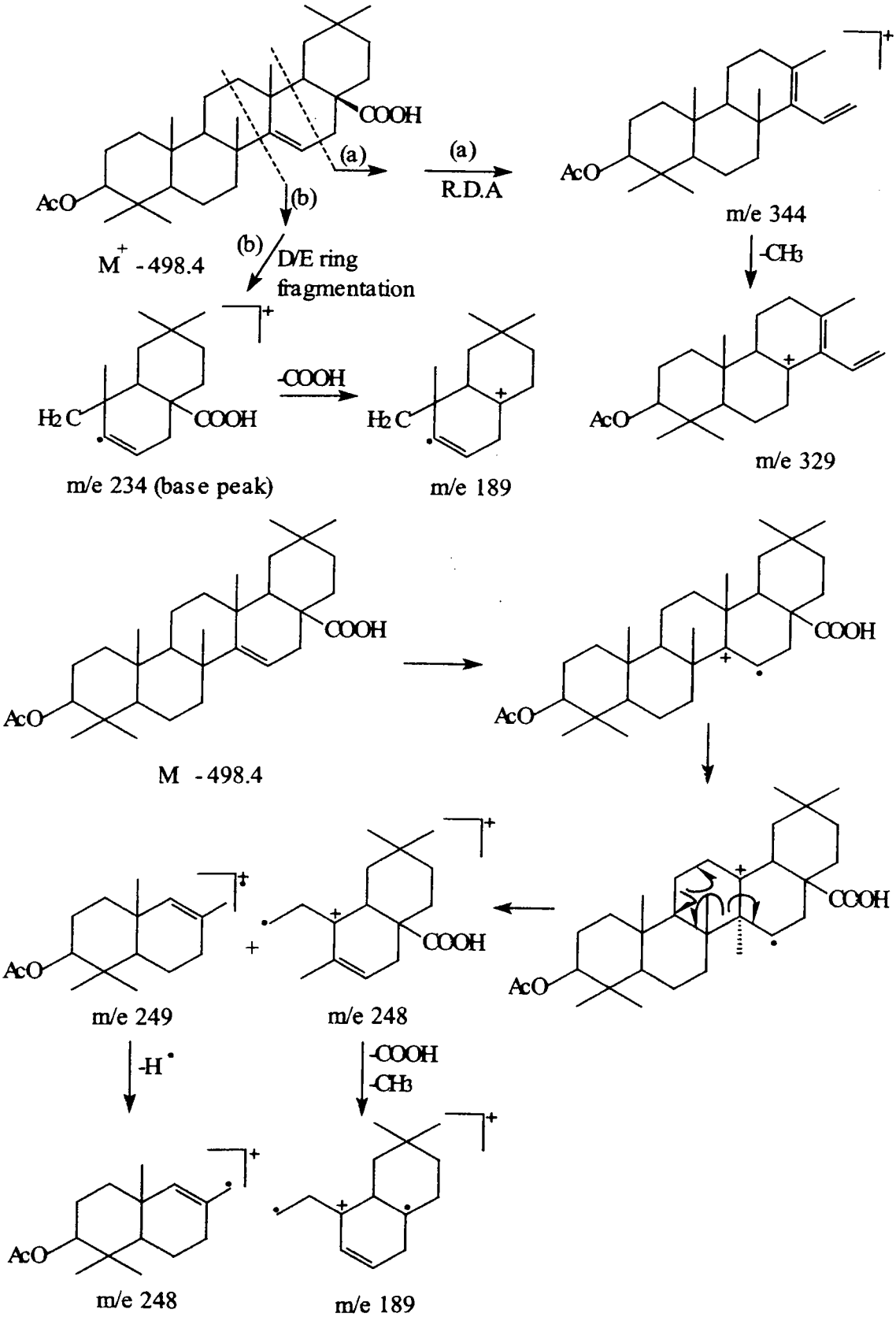
Taraxerol (7)

RESULTS AND DISCUSSION

The compounds **1** β-sitosterol, **2** stigmasterol, **3** 5(E) - eicosanoic acid (Boughton, et. al., 1952; Levin and Stuart Warren, 1988), **4** Gallic acid and **5** β-sitosterol-3-O-β-D-glucoside (Sakakibara, et. al., 1983; Atchutaramaiah, et. al., 1984) were obtained respectively through their spectral values from the methanol extract of heart wood of the plant *H .riparia*. Similarly the compounds **6** and **7** from the bark were chracterised and identified as taraxerone and taraxerol through their spectral values and by direct comparison with reported data (Corbett, et. al., 1972; Sakurai, et. al., 1987).

Compound **8** furnished colorless needles, m.p. 304-306°C was analysed as $C_{32}H_{50}O_4$ from the mass spectral data (EI and FAB mass). I.R spectrum showed strong absorptions at 1730 and 1240 cm^{-1} indicating the presence of acetoxy function, 3500 and 1688 cm^{-1} for the presence of carboxylic acid group and 832 cm^{-1} for a trisubstituted double bond. ^1H NMR spectrum showed a characteristic singlet at δ 2.04 assigned to acetoxy protons, a doublet by doublet centered at δ 5.54 (J = 8 and 4 Hz) indicating a proton on the trisubstituted double bond adjacent to methylene function. Another doublet by doublet resonated at δ 4.47 (J = 10 and 6 Hz) assigned to the ubiquitous 3 α methine proton geminal to the acetoxy function of triterpene skeleton. Seven tertiary methyls appeared as singlets in the region at δ 0.85 – 0.98. This data suggests that the compound **8** is a mono acetoxy pentacyclic triterpene mono carboxylic acid with a trisubstituted double bond. The position of the double bond was established by the mass spectral fragmentation. Compound **8** gave a molecular ion at m/z 498.4 in EI mass spectrum and further the FAB mass spectrum showed prominent peaks of M + Na^+ at 521.6, 2M + Na^+ at 1019.2, 3M + Na^+ at 1587.2 confirmed the M^+ ion of compound **8** is 498.4. The characteristic Retro - Diels Alder fragmentation ions noticed at m/e 344 and 329, and other fragment ions at m/e 234 and 189 by the cleavage of D/E and C/D ring of pentacyclic triterpene. This mass spectral data indicated the position of the double bond at 14-15 of the triterpene skeleton and similar to the taraxerane type triterpenes (Bruke and Le Quesene, 1971; Mc Phail, et. al., 1989; Budzkiewiez, et. al., 1963). The mass spectral fragmentation of compound **8** is depicted in Chart-**1.**

CHART - 1


COOH
AcO
(a)
(b)
R.D.A
m/e 344
-CH3
M+ -498.4
D/E ring fragmentation
-COOH
H2C
m/e 234 (base peak)
m/e 189
m/e 329
M -498.4
m/e 249
m/e 248
-H•
-COOH
-CH3
m/e 248
m/e 189

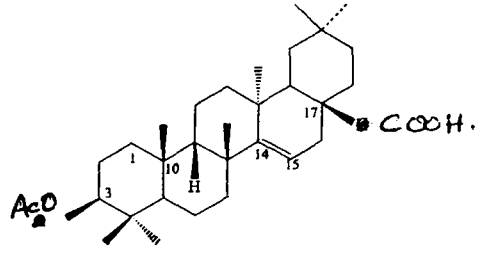
^{13}C NMR spectrum of compound **8** displayed 32 carbon resonances, analysed as seven methyls, ten methylenes, five methines and seven quaternary carbons form its APT spectrum. The signals at δ 184.29 and 171.01 indicate the presence of carboxylic acid and acetoxy carbonyl function. The resonances at δ 160.55 and 116.86 indicate the presence of double bond, which is a typical 14-15 double bond of taraxerane skeleton. Further, the C - H connectivities were noticed for acetoxy, olefinic methylene and methine protons from its HMQC spectrum. The ^{1}H, ^{13}C NMR and HMQC assignments are mentioned in **Table-1.** The above data infers that the compound **8** appears to be identical with the reported data of 3-Acetyl aleuritolic acid (Mc Lean, et. al., 1987).

Table -1

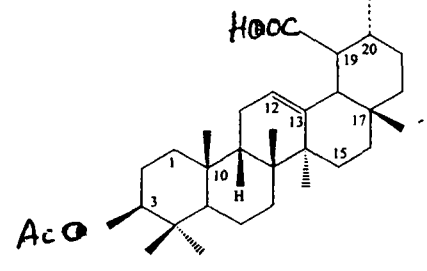
^{1}H NMR, ^{13}C NMR assignments and HMQC chemical shifts of (8)

Carbon No.	δ_C ($CDCl_3$)	δ_H ($CDCl_3$)	HMQC	
			^{13}C	Correlated proton signal
1	37.37	---	21.31	3-Ac, 2.04 (s)
2	23.46	---	33.32	12-H, 2.38 (m)
3	80.88	4.47 (1H, J= 10, 6 Hz)	35.32	19-H, 1.11, 1.25 (s)
			41.37	18-H, 2.29 (dd)
4	37.67	---	49.04	9-H, 1.42 (m)
5	55.58	0.88 (1H, m)	55.58	5-H, 0.88 (m)
6	18.73	---	80.88	3-H, 4.47 (dd)
7	40.73	---	116.56	15-H, 5.54 (dd)
8	39.03	---		
9	49.06	---		
10	37.93	---		
11	17.31	---		
12	33.32	---		
13	37.31	---		
14	160.55	---		
15	116.86	5.54 (1H, J = 8, 4 Hz)		
16	31.29	---		
17	51.51	---		
18	41.37	---		
19	35.32	---		
20	29.31	---		
21	33.66	---		
22	30.68	---		
23	27.96	0.89 (3H, s)		
24	16.59	0.85 (3H, s)		
25	15.65	0.95 (3H, s)		
26	26.21	0.95 (3H, s)		
27	22.47	0.92 (3H, s)		
28	184.29	---		
29	31.85	0.94 (3H, s)		
30	28.65	0.91 (3H, s)		
-$OCOCH_3$	171.01	---		
-$OCOCH_3$	21.31	2.04 (3H, s)		

In general, the triterpenoid class of derivatives are among the most common natural products isolated from the plants. However, they are difficult to characterize due to their extremely complex spectra, the large number of possible isomers and relative similarities of physical and spectral properties of different isomers. There has been plenty of confusion in the literature regarding structure and ^{13}C NMR assignments for 3 - Acetyl aleuritolic acid **8**.



(8)



(9)

3 – Acetyl aleuritolic acid **8** (m.p.278-281°C) was isolated for the first time from the bark of *Aleurites montana* and structure was established through ^{1}H NMR and mass spectral data (Mishra and Khastigar, 1970). Similar compound was isolated and identified as 3-Acetyl aleuritolic acid (m.p.301-302oC) from the seeds of *Phytolacca americana* (Bruke and Le Quesene, 1971; Won Sik Woo and Wagner, 1977), which had different melting point reported by previous workers in the literature. Also the same compound was isolated

from *Podadenia thwaitessi* (Carpenter, et. al., 1980) and ^{13}C NMR assignments were reported for the first time based on the comparison of previously assigned spectra for oleanolic acid derivatives. Subsequently, a similar compound was isolated from *Maprounea africana* (Wani, et. al., 1983) and altogether assigned different structure as 3 - Acetyl maprounic acid **9** having ursane skeleton, not taraxerane skeleton based on the high resolution mass and ^{1}H NMR values. Yet another triterpene acid was reported in literature from *Maprounea guianensis* (Mukharjee, et. al., 1984), which was initially assumed to be **9**, as its physical and spectral values were similar to the compound isolated by previous workers (Wani, et. al., 1983). But, the APT edited ^{13}C NMR and 2D NMR (^{1}H – ^{13}C shift correlations) spectral assignments differed from the previous data (Carpenter, et. al., 1980). Thus, the ^{13}C NMR values assigned to **8** in the literature were inappropriate. This led to the confusion of the structure of 3- Acetyl aleuritolic acid, whether having taraxerane skeleton **8** or ursane skeleton **9**. Finally this ambiguity was clarified by single crystal X- ray analysis of the compound obtained from *M. africana* and *M. guianensis* (Mc Phail, et. al., 1989) and revealed its identity as **8** not **9**, as reported by previous workers (Wani, et. al., 1983; Mukharjee, et. al., 1984).

Thus, the compound **8** was isolated from *H. riparia* as its physical and spectral properties are identical with the reported values (Won Sik. Woo and Wagner, 1977; Mc Lean, et. al., 1987; Mc Phail, et. al., 1989) and its identity was established as 3- Acetyl aleuritolic acid. Further, the compound 8 was hydrolysed with 0.5N KOH at room temperature gave a triterpene acid (m.p. 308-310°C) and readily identified as aleuritolic acid (Bruke and Le Quesene, 1971; Mc Phail, et. al., 1989). This triterpene acid and its derivatives isolated from *M. membranacea* (Beutler, et. al., 1995; Pengusparp, et. al., 1994) showed significant HIV-1 reverse transcriptase activity. The above results indicated that *H. riparia*, a medicinally important plant from Andhra Pradesh, India is another new source of bioactive triterpene acid **8**, and its HMQC correlations were also reported for the first time.

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