

New Triterpenoid Glycosides from the Stem Bark of *Samanea saman*



Nidhi Srivastava

Abstract: From the stem bark of *Samanea saman* two new triterpenoid glycoside have been isolated and characterized as $3\beta, 22\beta$ -dihydroxyolean-12-ene-24-O- β -D-xylopyranoside **1** and $1\beta, 2\alpha, 3\beta$ -trihydroxy-16 β -O-acetylolean-12-ene-28-oic-O [β -D-arabinopyranosyl (1 \rightarrow 3)]- β -D-arabinopyranoside **2** by spectral and chemical studies.

Keyword: *Samanea saman*, triterpenoid, glycoside

I. INTRODUCTION

Samanea saman (Mimosaceae) commonly called "Raintree" is a useful medicinal plant distributed from Yucatan Peninsula, Guatemala to Peru, Bolivia, Brazil, throughout the West Indies, in old world tropics and also in Southern Florida¹. It is used as an alcoholic source². It is used for cold, diarrhea, headache, intestine ailments, stomachach³, stomach cancer⁴, sore throat⁵. Earlier alkaloids, lupeol, lupeone, octacosanoic acid, hexacosanol, flavonoids, kaempferol⁶ have been isolated from the different parts of *Samanea saman*.

In continuation of our research on the chemical investigation of medicinal plants, we report herein isolation and structure elucidation of two new triterpenoid glycosides from *Samanea saman*.

The water insoluble portion of the hot ethanol extract of the air-dried crushed and defatted stem barks of *S. saman* on column chromatography yield compound **1** and **2**.

II. RESULT AND DISCUSSION

Compound **1** (C₃₅H₅₈O₇), a glycoside on acid hydrolysis gave D-xylose and an aglycone **1a**. The aglycone gave colour reactions 7-10 of unsaturated pentacyclitriterpenoid. It formed triacetate on acetylation showing the presence of three hydroxyl group. The IR spectrum of **1a** showed absorption for hydroxyl (3450 cm⁻¹), trisubstituted double bond (1630 cm⁻¹), primary and secondary alcoholic group (1250, 1100, 1050 cm⁻¹) and C-methyl (2900, 1385 and 1330 cm⁻¹) groups. The ¹H-NMR spectrum of **1a** showed signals for seven tertiary methyl groups at (δ 0.85, 0.95, 0.99, 1.03, 1.17, 1.31 and 1.35 (each 3H, S) and a vinyl proton at δ 5.25 (1H, t, J =3.3Hz) all of which suggested **1a** to be an olean-12-ene derivative.

The mass spectrum of **1a** revealed important peaks at m/z 234, 224, 210, 216, 204, 201 and 175 typical of retro-Diels-Alder fragmentation of ring-C of olean-12-ene derivative containing a hydroxyl group in ring A or B11.

Compound **1a** also gave positive Zimmermann test¹² suggesting the C-3 position for this hydroxyl group which was also biogenetically favoured.

The aglycone showed signal at δ 3.83 (1H, dd, J =9.6 Hz) with higher value of coupling constant confirming the β -orientation for hydroxyl group at C-3 (α or axial H)13.

The ion peak at m/z 216[234-H₂O] due to ready loss of water molecule showed the position of -OH group at C-22 which was also supported by the ¹³C-NMR signal at δ 75.6(d) for C-22. The ¹H-NMR signals at δ 4.35 and 4.52 (each 1H, d, J =12.1 Hz) were attributed to the methylene protons of hydroxymethyl group (AB system)¹⁴. Signal at δ 64.5 in ¹³C-NMR spectrum of **1a** confirmed the presence of CH₂OH group at C-24. Thus, aglycone **1a** was identified as $3\beta, 22\beta, 24$ -trihydroxyolean-12-ene.

The ¹H-NMR spectrum of **1** showed a signal for an anomeric proton at δ 4.98 (1H, d, J =6.5 Hz, H-1, xylose) and sugar protons at δ 3.2-3.8 (br, xylosyl protons) which was consistent with configuration of D-xylose. The β -type of glycosidic linkage was also confirmed by hydrolysis of **1** with the enzyme emulsin. The position of attachment of D-xylose at C-24 hydroxyl group was confirmed by down field signal at δ 74.5 (t) in the ¹³C-NMR of **1** for C-24. Thus the compound **1** was characterized as $3\beta, 22\beta$ -dihydroxyolean-12-ene-24-O- β -D-xylopyranoside.

Compound **2**, C₄₂H₆₈O₁₆ (M^+ 828), mp280°C, a non-reducing glycoside gave aglycone **2a** on acid hydrolysis with 7% H₂SO₄ and a sugar arabinose (Co-chromatographed with an authentic sample). Compound **2a**, C₃₂H₅₀O₇ (M^+ 546), gave colour reactions characteristic of unsaturated pentacyclitriterpenoid. Its IR spectrum showed absorption peaks for hydroxyl groups (3300 cm⁻¹), trisubstituted double bond (1640 cm⁻¹) and carboxylic group (3200 & 1700 cm⁻¹) and peak for -OCOCH₃ group (1690 & 1100 cm⁻¹). The ¹H-NMR spectrum of **2a** showed signals for seven tertiary methyl groups between δ 0.85-1.31 (each 3H, S), a vinylic proton at δ 5.34 (1H, t, J =3.4Hz) all of which suggested **2a** to be an olean-12-ene derivative.

In ¹H-NMR singlet at δ 2.03 (3H, S) shows the presence of -OCOCH₃ group. Which was also confirmed by singlet at δ 169.4 and quartet at δ 20.4 in ¹³C-NMR. On acetylation aglycone furnished tetraacetylated product and further methylation with diazomethane provided its monomethyl ester. These results clearly suggested the presence of three hydroxyl, one -OCOCH₃ and one acidic group in the aglycone **2a**.

Acetylated product of **2a** showed signals for three hydroxymethine protons signals in its ¹H-NMR spectrum at δ 3.22 (1H, d, J =10.7 Hz), 3.41 (1H, d, J =9.5 Hz) for H-1 and H-3, and at 4.03 (dd, 1H, J_1 =9.5 Hz and J_2 =10.7 Hz) for H-2 and for three acetoxymethine protons at δ 4.80 (1H, d, J_1 =10.5 Hz and J_2 =9.3 Hz) which were assigned as C-1 (or C-3), C-3 (or C-1) and C-2.

Revised Manuscript Received on March 10, 2020.

* Correspondence Author

Nidhi Srivastava*, Associate professor, Dept. of Chemistry, P.P.N. College, Kanpur, India. E-mail: nidhi.srivastava2006@gmail.com

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

New Triterpenoid Glycosides from the Stem Bark of *Samanea saman*

The *J* values of these signals indicated its trans-diaxial correlated protons of these three hydroxyl groups must be equatorial¹⁵.

The mass spectrum of aglycone showed the presence of both the groups (-COOH and -OCOCH₃) in ring D/E, peaks at *m/z* 306, 240 obtained due to retro Diels Alder fragmentation and subsequent fragments 261 (306-COOH), 247 (306-OCOCH₃), 202 (-COOH-OCOCH₃) and -COOH group must be present at C-16 and C-17, respectively. On comparing the ¹³C-NMR values of aglycone with 16 β -O-acetyl-28 oicacid¹⁶ confirmed the above result. The larger *J* value (δ 3.32, t, *J*=17.0 Hz) showed equatorial orientation of -OCOCH₃ group at C-16. On the basis of above facts **2a** was identified as 1 β , 2 α , 3 β -trihydroxy-16 β -O-acetylolean-12-ene-28-oic acid.

Easy hydrolysis of glycoside with acid as well as base¹⁷ [5N-NH₄OH] confirmed that sugar was attached by ester linkage. Quantitative estimation and molecular weight difference suggested the presence of two moles of sugar per mole of aglycone. ¹H-NMR spectrum of compound showed signals of two anomeric protons compound showed signals of two anomeric protons at δ 4.90 (1H, d, *J*=5.2 Hz) and 5.76 (1H, d, *J*=7.5 Hz). This confirmed that glycoside was disaccharide. On permethylation followed by acid hydrolysis permethylated derivative gave 2,4 di-*O*-methyl-D-arabinose and 2,3,4-trimethyl-*O*-D-arabinose. This confirmed that interglycosidic linkage was (1 \rightarrow 3).

The attachment of two sugar moieties were confirmed by comparing the ¹³C-NMR spectral data with **2** and **2a** which showed the attachment of sugar to C-28 by higher δ value at C-28 for **2** and lower δ value of **2a**. Hydrolysis of **2** with emulsion gave D-arabinose confirming the β -nature of glycosidic linkage.

From the above evidences the structure of compound **2** was determined as 1 β , 2 α , 3 β -trihydroxy-16 β -O-acetylolean-12-ene-28-oic-*O* [- β -D-arabinopyranosyl (1 \rightarrow 3)] - β -D-arabinopyranoside.

III. EXPERIMENTAL SECTION :

The stem bark of *Samanea saman* was collected in April, 1999 from the Botany Department, University of Allahabad, Allahabad, U.P., India. M.p.s measured in open capillary tube and are corrected. ¹HNMR and ¹³CNMR spectra were recorded on a JEOLUNK-A 500 spectrometer in CDCl₃ using TMS as an internal standard at 300 MHz and 100 MHz, respectively. IR spectra were run in KBr pellets. Mass spectra were recorded on JEOL SX 102/DA-6000 mass spectrophotometer.

The air-dried and finely crushed stem bark (5kg) of *Samanea saman* was repeatedly extracted with boiling EtOH (4x10l), concentrated under reduce pressure in a rotatory evaporator and poured into an excess of ice-cold distilled water with constant stirring to give reddish brown aqueous solution (fraction-I) and light brown residue (fraction-II) were obtained. The water insoluble portion was extracted successively with different solvents of increasing polarity over a sintered Column. Elution with solvent system C₆H₆ : EA (9:1, v/v) followed by running in preparative TLC using benzene:chloroform (9:1, v/v) marked with the help of UV lamp gave compounds **1** (0.69g), and from pure ethyl acetate followed by running in preparative TLC using ethylacetate : methanol(9:1, v/v), compound **2** (0.35g) were obtained.

Compound **1**, mp. 136^oC, yield 690 mg, homogenous on TLC, R_f 0.46 solvent C₆H₆:CHCl₃ (9:1, v/v); Anal. Found: C, 71.10; H, 9.82; Calcd. for C₃₅H₅₈O₇ : C, 71.15; H, 9.89% . IR (KBr) 3450, 2923, 1630, 1100, 1050. ¹HNMR (CDCl₃, 300 MHz) : δ 0.85 (s, 3H, H-25), 0.95 (s,3H, H-26), 0.99 (s,3H, H-29), 1.03 (s,3H, H-30), 1.17 (s,3H, H-27), 1.31 (s,3H, H-28), 1.35 (s,3H, H-23), 2.59 (brs,1H, *J*=13Hz), 3.83 (dd, 1H, *J*=9.6 Hz, β -OH at C-3), 5.25 (t, 1H, *J*=3.3 Hz), 4.35 and 4.52 (d, 1H, *J*=12.1 Hz for -CH₂OH group proton), 4.98 (d, 1H, *J*=7 Hz for β linkage) and 3.2-3.8 (m, 5H, sugar protons); MS : *m/z* 588[M⁺], 458, 427, 409, 391, 234, 224, 219, 216, 204, 201, 175, 119; ¹³C-NMR data are given in **Table-I**.

Compound **2**, mp. 280^oC, yield 350mg, homogenous on TLC, R_f 0.64 solvent CHCl₃ :MeOH (8:2, v/v); Anal. found : C, 59.99; 8.23; Calcd for C₄₂H₆₈O₁₆ : C, 60.85; H, 8.24%; IR (KBr) 3300, 3200, 1700, 1690, 1640, 2933, 1381, 1362, 1100, 970; ¹HNMR (CDCl₃, 300 MHz) : δ 0.85 (s, 3H, H-25), 0.93 (s, 3H, H-26), 0.95 (s, 3H, H-29), 1.04 (s, 3H, H-30), 1.17 (s, 3H, H-27), 1.24 (s, 3H, H-28), 1.31 (s, 3H, H-23), 2.03 (s, 3H, -OCOCH₃), 5.34 (t, 1H, *J*=3.4 Hz), 4.80 (d, 1H, *J*=10.5 Hz), 4.88 (d, 1H, *J*=9.3Hz), 5.20 (dd, 1H, *J*=10.5 and 9.3 Hz), 3.22 (d, 1H, *J*=10.7Hz, H-1), 3.41 (d, 1H, *J*=9.5 Hz, H-3), 4.03 (dd, 1H, *J*=10.7 and 9.5 Hz, H-2), 4.90 (d, 1H, *J*=5.2 Hz), 5.76 (d, 1H, *J*=7.5Hz), 3.25-3.85 (m, 10H, sugar protons); MS : *m/z* 828 [M⁺], 546, 306, 261, 247, 240, 202; ¹³CNMR data are given in **Table-II**.

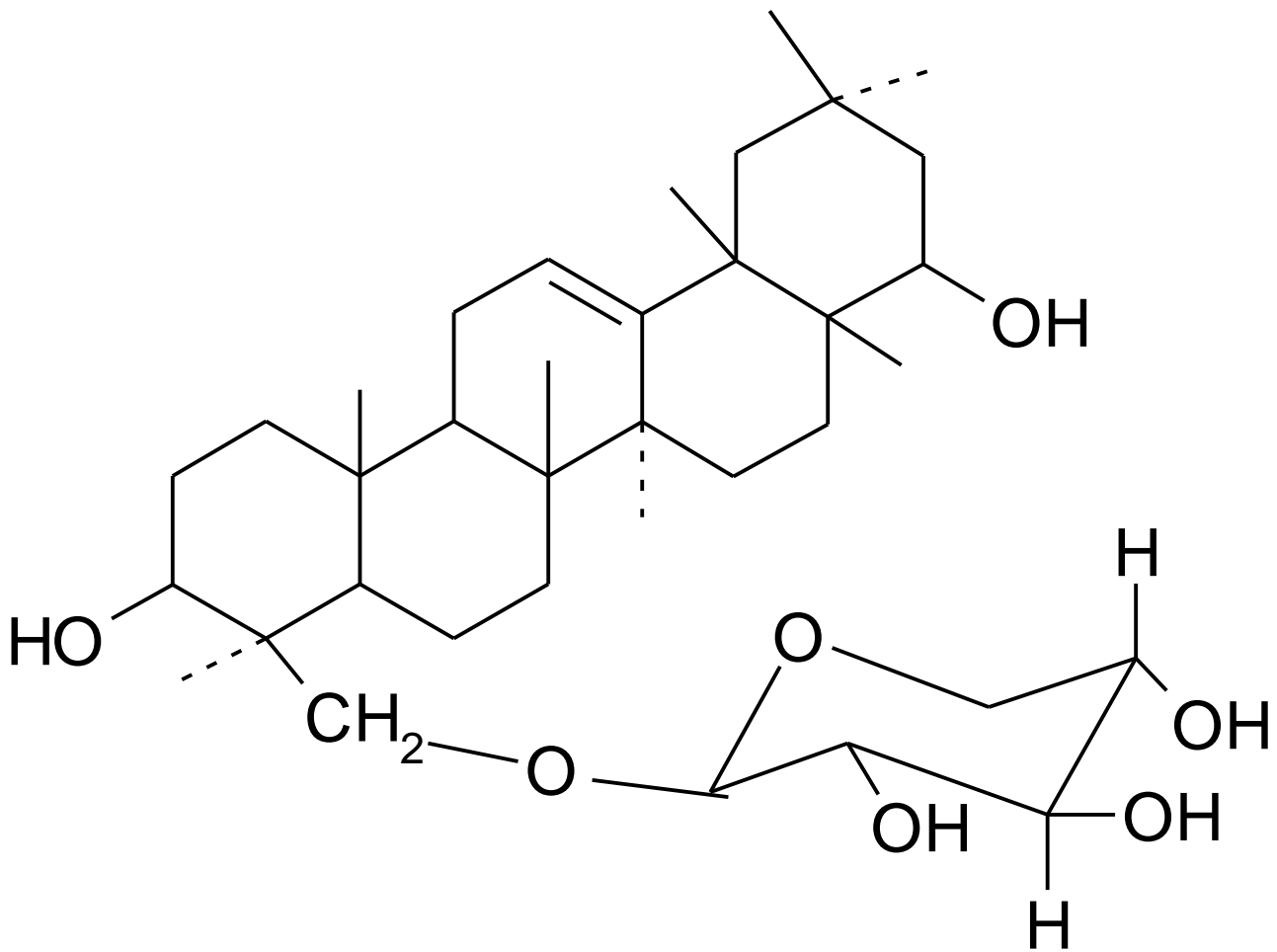
IV. CONCLUSION:

In conclusion *Samanea saman* is a rich source of triterpenoid. Triterpenoid are of great interest due to many biological activity and several parts of the plants have a particular pleasant smell. This smell is due to the presence of certain volatile oil known as essential oil. Among the chief constituent of essential oil are triterpenoid upto C₁₅. Due to their biological activity and characteristic smell, plants are used in pharmacy and perfumery industry respectively.

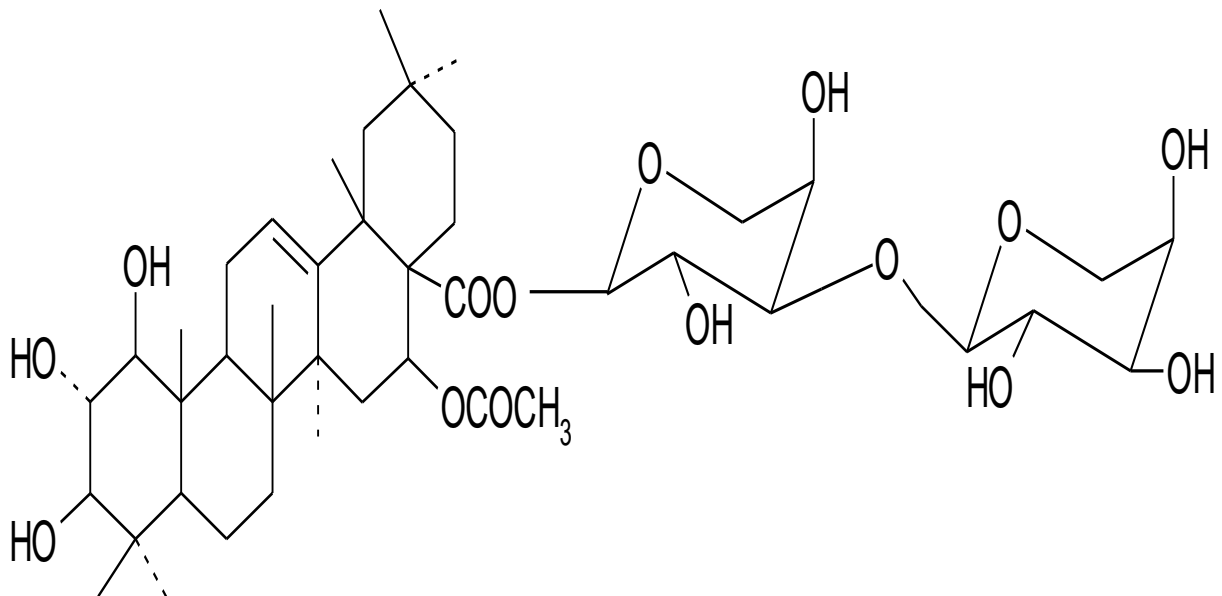
REFERENCES

1. James Duke, A, *Handbook of Energy Crop*, 1983.
2. CSIR (Council of Scientific and Industrial Research) *The Wealth of India*, New Delhi, 11, 1948-1976.
3. Duke, J.A. & Wain KK, *Medicinal Plants of the World*, 3, 1981.
4. Hartwell JL, *Plants used against Cancer*, A survey Lloydia, 30-34, 1967-1971.
5. Ayensu, ES, *Medicinal Plants of the West Indies*, Reference Publications, Inc., Algonac, MI, 1981, 282.
6. List PH and Horhamner L, *Hager's handbuchderpharmazeutischen praxis*, Springer, Verlag, Berlin, 2-6, 1969-1979.
7. Liebermann C, *Ber Deutsch Chem. Ges.*, 1885, 1804.
8. Takahashi K, Kawashi S, NishimuraKT, Kutota K, Tanabe Y and Takani M, *Chem Pharm Bull*, 22, 1974, 650.
9. Brieskorne CH and Briner B, *Pharm ActaHelv*, 28, 1953, 139.
10. Ruzicka L and Leibigs, *Ann Chem*, 25, 1929, 471.
11. Takahashi K, Tanka O and Shibata S, *Phytochemistry*, 8, 1969, 2345.
12. Barton DHR and De Mayo P, *J ChemSoc.*, 1954, 887.
13. Rogers OB and Subramony G, *Phytochemistry*, 27, 1988, 531.
14. Sanghi R, Tripathi K and Sharma JP, *Indian J Chem*.39B, 2000, 477.
15. Srivastava M and Singh J, *Int. J. Pharmacoy*, 32, 1994, 197.
16. Rai R, Gupta A, Chauhan D, Purwar C and Singh J, *Pharmaceutical Biology*, 39, 2001, 413.
17. Hariharam V and Rangaswami S, *Phytochemistry*, 9, 1970, 409.





3β, 22β-dihydroxyolean-12-ene-24-O-β-D-xylopyranoside1



1β, 2α, 3β-trihydroxy-16β-O-acetylolean-12-ene-28 oic acid-28-O-[-β-D-arabinopyranosyl (1→3)]-β-D-arabinopyranoside2

New Triterpenoid Glycosides from the Stem Bark of Samanea Saman

Table –I. ¹³C-NMR (δ) values of glycoside SS-1 and its aglycone

Chemical Assigned	Glycoside Chemical Shift (ppm)	Aglycone Chemical shift (ppm)
C-1	38.6 (t)	39.0(t)
C-2	27.5(t)	28.4(t)
C-3	80.0 (d)	79.8(d)
C-4	43.0 (s)	43.0(s)
C-5	57.0(d)	56.3(d)
C-6	19.2(t)	19.4(t)
C-7	33.7(t)	33.5(t)
C-8	40.1(s)	39.9(s)
C-9	48.6(d)	48.1(d)
C-10	36.8(s)	37.0(s)
C-11	24.6(t)	24.0(t)
C-12	123.0(d)	122.4(d)
C-13	145.0(s)	144.9(s)
C-14	42.0(s)	42.3(s)
C-15	26.0 (t)	26.4(t)
C-16	29.4 (t)	29.0(t)
C-17	37.5 (s)	38.4 (s)
C-18	44.5(d)	44.8(d)
C-19	41.9 (t)	41.5 (t)
C-20	30.5(s)	30.0(s)
C-21	37.0(t)	37.3(t)
C-22	75.6(d)	75.6(d)
C-23	23.1(q)	23.5(q)
C-24	74.5 (t)	64.5 (t)
C-25	16.2(q)	16.3(q)
C-26	17.5(q)	17.1(q)
C-27	26.8(q)	25.5(q)
C-28	21.1(q)	21.1(q)
C-29	32.5(q)	32.0(q)
C-30	24.6(q)	24.4(q)
C-1'	103.6(q)	
C-2'	71.5 (q)	
C-3'	75.2 (d)	
C-4'	70.1 (d)	
C-5'	67.6 (t)	

Table –II. ¹³C-NMR (δ) values of glycoside SS-2 and its aglycone

Chemical Assigned	Glycoside Chemical Shift (ppm)	Aglycone Chemical shift (ppm)
C-1	74.6 (d)	74.4 (d)
C-2	74.8 (d)	74.8 (d)
C-3	76.5 (d)	76.3(d)
C-4	43.2(s)	43.2(s)
C-5	57.2 (d)	57.3(d)
C-6	19.2(t)	19.2(t)
C-7	33.6(t)	33.6(t)
C-8	40.2(s)	40.1(s)
C-9	48.4(d)	48.4(d)
C-10	36.8(s)	36.8(s)
C-11	24.6(t)	24.6(t)
C-12	124.2(d)	124.2(d)
C-13	146.1(s)	146.1(s)
C-14	42.0(s)	42.0(s)
C-15	26.3(t)	26.3(t)
C-16	81.4(d)	81.4(d)
C-17	48.5(s)	48.5(s)
C-18	42.6(d)	42.6(d)
C-19	39.6(t)	39.5(t)
C-20	36.8(s)	36.6(s)
C-21	37.3(t)	37.4(t)
C-22	38.2(t)	38.2(t)
C-23	23.2(q)	23.2(q)
C-24	17.6(q)	17.6(q)
C-25	16.1(q)	16.1(q)
C-26	17.5(q)	17.5(q)
C-27	26.8(q)	26.8(q)
C-28	181.9(s)	179.2(s)
C-29	27.4(q)	27.3(q)
C-30	17.9(q)	
OCOCH ₃	20.5(q)	
OCOCH ₃	168.7(s)	

C-1'	105.6(d)	
C-2'	73.8(d)	
C-3'	74.6(d)	
C-4'	70.2(d)	
C-5'	67.0(t)	
C-1'	104.5(d)	
C-2'	73.0(d)	
C-3'	72.1(d)	
C-4'	70.0(d)	
C-5'	67.5(t)	

AUTHORS PROFILE



Dr. Nidhi Srivastava is Associate Professor & Head of the Department of Chemistry in P.P.N college Kanpur, affiliated to CSJM University, Kanpur. She obtained his graduation, post-graduation and D.Phil degree from University of Allahabad, Allahabad. She qualified JRF (NET)-2001 and MP (SLET)-2000. And also work as SRF(CSIR) for two years. She has a long teaching experience of UG and PG classes from last 20 years. Her field of research mainly includes isolation of natural products their identification characterization and screening effect. Dr. Nidhi Srivastava has participated and delivered lectures at various seminars, conferences. She is also a member of several professional societies.