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REVIEW

Coumarinolignoid-A Rare Natural Product: A Review†

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Coumarinolignoids are naturally occurring compounds that are popular as antihepatotoxic agent and will be interesting future molecules for antitumor and anticancer activities. In this review article, we summarize the isolation, extensive spectroscopic data, syntheses and biological significance of coumarinolignoids along with their regioisomers from the discovery till October 2010. These naturally occurring compounds are obtained from medicinal plants and exhibit strong biological activities.

Key Words: Coumarinolignoids, Isolation, Spectral data, Syntheses, Biological activities.

INTRODUCTION

Heterocycle plays an important role in the pharmaceutical field. Their importance can hardly be overemphasize and justifies a long lasting effort to work out new synthetic protocols for their production. Natural products impart medicinally significant heterocycles from the earlier inventions. New bioactive natural products always gain appreciable attention of researchers due to their minimum or no side effects. Coumarinolignoids (**A**) are one of these proven natural bioactive compounds particularly as hepatoprotective agents (Fig. 1). These are very few and rare group of naturally occurring organic compounds consisting of C_6-C_3-C_6 units[1]. In the novel skeleton of coumarinolignoid, the coumarin moieties are linked with the phenyl propanoid units through a 1,4-dioxane bridge[1]. This was earlier witnessed in the flavonolignoids (sylibin)[2] and xanthonolignoid (kielcorin)[3,4]. Phenylpropanoid moiety usually has one or several C_6-C_3 units that are widely distributed in nature.

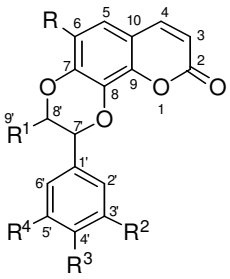


Fig. 1. Coumarinolignoid A

This article presented a detailed coverage about isolation and syntheses of coumarinolignoids along with their potential biological activities. Furthermore, complete physical and spectral information is also provided.

Isolation: The isolation reported herein covers all the natural sources from which this class of compound was discovered. The structure of all naturally occurring coumarinolignoids were established on the basis of their spectral evidences (Tables 1 and 2).

In 1980, first coumarinolignoid cleomiscosin A (**1**) was isolated from *Cleome viscose* seeds by Chattopadhyay and coworkers[5]. Ray *et al.*[6] reported the isolation of cleomiscosin B (**3**), a regioisomer of **1**, from the same plant. Moreover, compound **3** was also isolated from the roots of *Hannoa klaineana*[7]. Ichino *et al.*[8] studied the liver protective property of cleomiscosin B.

Coumarinolignoid **1** was also isolated from its new sources *Simaba multiflora*[9], *Soulamea soulameoides*[9], *Matayba arborescens*[9], *Aesculus turbinate*[8], *Coptis japonica*[10], *Hannoa klaineana*[7], *Protium heptaphyllum*[11] and *Jatropha gossypifolia*[12]. The spectroscopic evidences have brought on the revision of the structure of cleomiscosin A as **1** and **3** (Fig. 2, Tables 3 and 4).

Zoghbi *et al.*[13] explored a new coumarinolignoid alongwith its regioisomer, propacin (**2, 30**) from *Protium opacum* in 1981. Their structures were elucidated on the basis of chemical and physical evidences. These compounds were also reported from the roots of *Jatropha glandulifera* by Parthasarathy *et al.*[14] in 1984 and *Jatropha gossypifolia* by Venkataiah *et al.*[15] in 2001.

†Dedicated to Prof. Dr. Bushra Mateen on her 68th Birthday.

TABLE-1
PHYSICAL AND SPECTRAL CHARACTERISTICS OF COUMARINOLIGNOIDS

Compound	m.p. (ºC), $[\alpha]_D$	IR ν_{max} (cm^{-1})	UV-VIS λ_{max} (nm)	MS *m/e* (rel. int. %)
1 $C_{20}H_{18}O_8$, 386	247º[20], ± 0º (c 0.1 CH_3OH)	3500, 1720, 1620, 1580	EtOH: 288, 327 (ε 5661, 10550)	386(52), 368(18), 354(14), 249(18) 208(48), 180(94), 162(20), 151(10), 37(100), 124(54)
1 diacetate $C_{24}H_{22}O_{10}$, 470	175º[20]	1765, 1730, 1718, 1610, 1575	-	470(76), 428(36), 68(100), 369(25), 222(87), 179(31), 149(15), 131(16)
2 $C_{20}H_{18}O_7$, 370	238-241º[39], -	3400, 1710, 1615, 1565, 1450, 1290, 1145, 1050, 840	MeOH: 231, 257, 286, 323 (ε 33000, 4650, 7800, 13950)	370(40), 327(10), 233(30), 164(100)
2 acetate $C_{22}H_{20}O_8$, 412	203-204º[39]	1770, 1730, 1640, 1610, 1470, 1320, 1225, 1160, 1065, 850	-	412(M^+), 370, 328, 233, 206, 164, 149
3 $C_{20}H_{18}O_8$, 386	275-278º[34] ± 0º (c = 0.1, CH_3OH)	3510, 1720, 1610, 1560	EtOH: 285, 328	386(48), 368(2), 208(5), 180(100), 137(85), 124(48)
3 diacetate $C_{24}H_{22}O_{10}$, 470	174º[20]	1762, 1730, 1718, 1612, 1570	-	-
4 $C_{20}H_{18}O_8$, 386	235-238º[16] ± 0º (c = 0.92, C_5H_5N)	3480, 3210, 1730, 1610, 1570, 1450, 1340, 1270, 1115, 1055, 835	MeOH: 242, 260, 317, (ε 9170, 8892, 11230)	386(6), 368(5), 354(9), 311(5), 210(50), 178(100), 167(60), 150(58)
4 diacetate $C_{24}H_{22}O_{10}$, 470	206-208º[37], -	1720, 1610, 1570	-	470, 428 (100), 368, 252
5 $C_{21}H_{20}O_9$, 416	255º[20] ± 0º (c = 0.1, CH_3OH)	3420, 1720, 1685	MeOH: 232, 280, 322, 258, 292, 328 (ε 25600, 4160, 12160)	416(7), 249(5), 210(56), 208(45), 193(21), 180(34), 167(100), 149 (50), 37(76), 109(50), 91(49), 79(78)
6 $C_{20}H_{18}O_8$, 386	220º[21], -	3520, 1710	MeOH: 260, 295, 340	386(100), 355(4.02), 354(6.23), 353(6.28), 327(11.23), 210(53.31), 192(85.87), 191(55.20), 180(20.13), 178(16.51), 177(18.50), 167(68.05), 154(16.98), 149(18.38), 149(21.06)
6 acetate	210º[21]	-	-	-
7 $C_{21}H_{20}O_9$, 416	238-239º[22], -	3470, 1735, 1620, 1460, 1229, 1120, 1040, 820	MeOH: 240, 320	416, 398, 210, 208, 182, 167, 154
7 diacetate	190º[22]	-	-	-
8 $C_{26}H_{28}O_{13}$, 548	254-255º[23], +23.5 (c = 0.1, DMSO)	3440, 3245, 1720, 1620, 1575, 1442, 1330, 1265	MeOH: 240, 265, 322 (ε 9150, 8790, 11310)	386(8), 368(6), 354(10), 311(15), 210(70), 178(100), 167(65), 150(75)
8 acetate $C_{36}H_{38}O_{18}$, 758	-	1725, 1625, 1570, 1450, 1355, 1210	-	-
9 $C_{20}H_{18}O_9$, 402	245-246º[25], -	3541, 3446, 1705, 1620, 1577, 1525, 1446, 1421, 1306, 1198, 1130, 1086, 1063, 852, 752.1	-	402, 384, 344, 311, 249, 219, 208(100), 196, 168, 153, 109, 81, 63, 51
10 $C_{22}H_{20}O_9$, 428	-, ±0º (c = 0.02, CH_3OH)	3430, 2934, 1721, 1630, 1591	MeOH: 285, 326 (ε 3.62, 4.09)	386(69), 208(46.1), 180(69.57), 137(100)
11 $C_{23}H_{22}O_9$, 442	-, ± 0º (c = 0.01, CH_3OH)	3432, 2935, 1720, 1629, 1590	MeOH: 289, 329 (ε 3.78, 4.03)	386(70), 208(44.4), 194(65), 151(100)
12 $C_{23}H_{22}O_{10}$, 458	-, ± 0º, (c = 0.01, CH_3OH)	3433, 1721, 1628, 1585	MeOH: 233, 323 (ε 3.28, 4.10)	386(73), 208(44.8), 210(53.6), 167(100)
13 $C_{20}H_{18}O_8$, 386	-, 15.5º (c = 0.1, C_5H_5N)	3380, 2923, 2852, 1710, 1648, 1614, 1573, 1518, 1452, 1416, 1150	MeOH: 329, 219, 214 (ε 2.09, 2.53, 2.04)	137(86), 180(144), 208(10), 354(2), 368(6), 368(2)
14 $C_{26}H_{28}O_8$, 468	-, 0º (c = 0.48, $CHCl_3$)	3440, 1710, 1615, 1580, 1520, 1500, 1460, 1400, 1350, 1310, 1220, 1140, 1110	MeOH: 328, 235, 220 (ε 4.67, 4.91, 5.01)	469(69), 468(100), 303(20), 302(99), 279(49), 265(28)
15 $C_{29}H_{32}O_7$, 492	-, 0º (c = 5.05, $CHCl_3$)	3430, 1710, 1615, 1580, 1520, 1460, 1400, 1300, 1280, 1235, 1200, 1140, 1070	MeOH: 331, 289, 232, 223 (4.77, 4.50, 5.00, 5.00)	492(100), 425(13), 424(51), 423(89), 395(23), 394(77), 363(16), 356(46), 287(58), 277(11), 276(52), 261(26)
16 $C_{29}H_{32}O_7$, 492	-, 0º (c = 0.53, $CHCl_3$)	3420, 1710, 1615, 1580, 1515, 1460, 1400, 1310, 1270, 1235, 1200, 1135, 1070	MeOH: 332, 288, 235, 219 (4.21, 3.98, 4.50, 4.60)	493(31), 492(100), 25(23), 424(52), 423(23), 422(21), 396(18), 395(66), 363(16), 327(16), 287(29), 276(21), 260(13)
17 $C_{28}H_{30}O_7$, 478	-, -	-	-	478(2), 407(54), 379(20), 355(18), 276(714), 261(39), 233(82), 221 (100), 189(63), 61(81), 128(81), 115(70)
18 $C_{21}H_{20}O_8$, 400	-, -	2944, 1605, 1520-1404, 1154-1137, 3394	-	400, 263, 164, 137`

Compound	m.p. (ºC), $[\alpha]_D$	IR ν_{max} (cm^{-1})	UV-VIS λ_{max} (nm)	MS *m/e* (rel. int. %)
19 $C_{19}H_{16}O_9$, 388	258-259^{o30}, ± 0º (c = 0.50, CH_3OH)	3433, 2929, 1693, 1621, 1572, 1500, 1463, 1425, 1323, 1213, 1158, 847	MeOH: 322, 252, 237	-
20 $C_{19}H_{16}O_9$, 388	285-286^{o30}, ± 0º (c = 0.50, CH_3OH)	3433, 2929, 1693, 1621, 1572, 1500, 1463, 1425, 1323, 1213, 1158, 847	MeOH: 323, 254, 232	-
21 $C_{20}H_{18}O_9$, 402	275-276^{o30}, ± 0º (c = 0.50, CH_3OH)	3400, 2930, 1683, 1615, 1572, 1500, 1447, 1419, 1342, 1228, 1134, 853	MeOH: 327, 254, 228	-
22 $C_{20}H_{18}O_9$, 402	-, -0.7º (c = 0.1, CH_3OH)	3349, 1705	-	-
23 $C_{29}H_{24}O_{10}$, 532	-, -	1590, 1720, 1715, 2930, 3430	286, 328 (solvent not mention)	386, 208, 180, 137
24 $C_{30}H_{26}O_{11}$, 562	-, -	Same as **23**	Same as **23**	Same as **23**
25 $C_{29}H_{24}O_{11}$, 548	-, -	Same as **23**	Same as **23**	Same as **23**
26 $C_{28}H_{24}O_{12}$, 552.13	-, -	Same as **23**	Same as **23**	Same as **23**
27 $C_{21}H_{20}O_9$, 428	120-121^{o24}, ± 0º (c= 0.4687, $CHCl_3$)	3424, 1720, 1615, 1574	EtOH: 322 (ε 3.63)	-
28 $C_{21}H_{20}O_9$, 416	258^{o40}, ±0º (c = 0.1, CH_3OH)	3420, 1715, 1690, 1610, 1580	-	416(100), 249, 210, 208, 182, 180, 167, 154, 149

TABLE-2
^{1}H AND ^{13}C NMR OF COUMARINOLIGNOIDS

1 *Cleome viscose*[20, 35]	^{1}H NMR δ (C_5D_5N): 3.74, 3.82 (2s, 2 × OMe), 3.94 (dd, *J* = 13, 3 Hz, Ha-9'), 4.35 (dd, *J* = 13, 2 Hz, Hb-9'), 4.5 (m, H-8'), 5.01 (br s, OH), 5.62 (d, *J* = 8 Hz, H-7'), 6.49 (d, *J* = 9.5 Hz, H-3), 6.78 (s, H-5), 7.22-7.56 (m, H-2', H-5' and H-6'), 7.32 (br s, OH), 7.8 (d, *J* = 9.5 Hz, H-4); ^{13}C NMR δ (C_5D_5N): 160.8 (C-2), 113.6 (C-3), 144.5 (C-4), 101.1 (C-5), 146.3 (C-6), 138.4 (C-7), 133.0 (C-8), 139.3 (C-9), 111.9 (C-10), 127.5 (C-1'), 112.3 (C-2'), 150.0 (C-3'), 149.0 (C-4'), 116.6 (C-5'), 121.7 (C-6'), 77.5 (C-7'), 79.9 (C-8'), 60.7 (C-9'), 55.8 (OMe), 56.2 (OMe)
Synthetic	^{1}H NMR δ ($CDCl_3$): 2.06 (s, OAc), 2.31 (s, OAc); ^{13}C NMR δ ($CDCl_3$): 20.6q, 168.5s, 170.2s, 20.6q (2 × OAc)
2 *Protium opacum* [13, 39]	^{1}H NMR δ ($CDCl_3$): 6.33, 7.63 (d, *J* = 9 Hz, H-3, H-4), 6.55 (s, H-5), 6.93 (s, H-2', H-5', H-6'), 4.7 (d, *J* = 7.5 Hz, H-7'), 4.3 (m, H-8'), 1.33 (d, *J* = 6.5 Hz, Me-8'), 3.95, 3.9 (2s, 2 OMe); ^{13}C NMR δ (DMSO-d_6): 159.9 (C-2), 113.1 (C-3), 144.7 (C-4), 100.8 (C-5), 147.3 (C-6), 137.3 (C-7), 131.3 (C-8), 149.2 (C-9), 111.2 (C-10), 126.8 (C-1'), 111.9 (C-2'), 145.1 (C-3'), 147.7 (C-4'), 115.4 (C-5'), 120.8 (C-6'), 80.1 (C-7'), 73.2 (C-8'), 16.7 (C-9') 55.8 (2 × OMe)
Synthetic	^{1}H NMR δ ($CDCl_3$): 7.1-7.07 (m, H-5', H-6'), 2.33 (s, OAc)
3 *Cleome viscose*[6, 20]	^{1}H NMR δ (C_5D_5N): 7.44 (d, *J* = 2.0 Hz, H-2'), 6.42 (d, *J* = 9.5 Hz, H-3), 7.75 (d, *J* = 9.5 Hz, H-4), 6.76 (s, H-5), 7.31 (d, *J* = 8.1 Hz, H-5'), 7.36 (dd, *J* = 2.0, 8.1 Hz, H-6'), 4.54 (d, *J* = 8.0 Hz, H-7'), 5.55 (d, *J* = 8.0 Hz, H-8'), 3.94 (dd, *J* = 12.8, 3.5 Hz, H-9'), 4.29 (dd, *J* = 12.8, 2.3 Hz, H-9'), 3.72, 3.84 (s, 2 × OMe); ^{13}C NMR δ (C_5D_5N): 160.7 (C-2), 113.8 (C-3), 144.4 (C-4) 101.2 (C-5), 146.2 (C-6), 138.1 (C-7), 133.2 (C-8), 139.4 (C-9), 111.8 (C-10), 127.5 (C-1'), 112.3 (C-2'), 150.1 (C-3'), 149.1 (C-4'), 116.5 (C-5'), 121.7 (C-6'), 77.1 (C-7'), 80.2 (C-8'), 61.1 (C-9'), 55.9, 56.1 (2 × OMe)
Synthetic	^{1}H NMR δ ($CDCl_3$): 3.84 (s, OAc), 3.92 (s, OAc); ^{13}C NMR δ ($CDCl_3$): 170.2 s, 168.6 s, 20.2 q, 20.6 q
4 *Daphne tangutica* [16, 37]	^{1}H NMR δ (DMSO-d_6): 3.48 (m, H-9), 3.78 (s, 2 × OMe), 4.32 (m, H-8), 5.03 (d, *J* = 8 Hz, H-7), 6.31 (d, *J* = 9.5 Hz, H-3), 6.75 (s, H-2 and H-6), 6.94 (d, *J* = 9 Hz, H-6), 7.18 (d, *J* = 9 Hz, H-5), 7.96 (d, *J* = 9.5 Hz, H-4), 8.55 (br s, OH); ^{13}C NMR δ (C_5D_5N): 160.4 (C-2), 113.6 (C-3), 144.3 (C-4), 119.8 (C-5), 113.2 (C-6), 147.6 (C-7), 138.4 (C-8), 149.2 (C-9), 113.6 (C-10), 126.4 (C-1'), 106.3 (C-2'), 149.2 (C-3'), 132.2 (C-4'), 149.2 (C-5'), 106.3 (C-6'), 77.8 (C-7'), 79.9 (C-8'), 60.7 (C-9'), 56.4, 56.4 (2 × OMe)
Synthetic	^{1}H NMR δ ($CDCl_3$): 2.03 (s, aliph. Ac), 2.29 (s, ar Ac); ^{13}C NMR δ ($CDCl_3$): 170.2s, 168.5s, 20.5q, 20.6q
5 *Cleome viscose*[20]	^{1}H NMR δ (DMSO-d_6): 6.36 (d, *J* = 9 Hz, H-3), 7.98 (d, *J* = 9 Hz, H-4), 6.93 (s, H-5), 6.76 (s, H-2'), 6.76 (s, H-6'), 4.98 (d, *J* = 8 Hz, H-7'), 4.38 (m, H-8'), 3.68 (dd, *J* = 12.5, 7 Hz, H-9'), 3.41 (dd, *J* = 12.5, 3.5 Hz, H-9'), 3.79 (s, OMe), 3.77 (s, OMe); ^{13}C NMR δ (C_5D_5N): 160.8 (C-2), 113.7 (C-3), 144.5 (C-4), 101.0 (C-5), 146.3 (C-6), 138.1 (C-7), 133.5 (C-8), 139.2 (C-9), 111.9 (C-10), 126.3 (C-1'), 106.1 (C-2'), 149.1 (C-3'), 135.5 (C-4'), 149.1 (C-5'), 106.1 (C-6'), 77.7 (C-7'), 79.7 (C-8'), 60.7 (C-9'), 56.2, 56.4 (2 × OMe)
6 *Aleurrites moluccana*[21]	^{1}H NMR δ (DMSO-d_6): 3.60 (m, H-9'), 3.85 (s, 2 × OMe), 4.35 (m, H-8'), 5.11 (d, *J* = 8 Hz, H-7'), 6.36 (d, *J* = 9 Hz, H-3), 6.8 (s, H-2' and H-8'), 7.04 (s, H-8), 7.36 (s, H-5), 7.99 (d, *J* = 9 Hz, H-4)
Synthetic	^{1}H NMR δ ($CDCl_3$): 2.08 (s, OAc), 2.35 (s, OAc); ^{13}C NMR δ ($CDCl_3$): 160.92 (C-2), 114.45 (C-3), 142.70 (C-4), 114.30 (C-5), 139.90 (C-6), 146.7 (C-7), 105.04 (C-8), 149.3 (C-9), 113.20 (C-10), 20.50 (MeCOOC-9), 132.90 (C-1'), 103.70 (C-2', C-6'), 152.1 (C-3', C-5'), 129.50 (C-4'),77.20 (C-8'),62.30 (C-9'),20.30 (MeCOOC-4').168.2 (MeCOOC-4'), 170.1 (MeCOOC-9'), 56.10 (2 × OMe)
7 *Aleurites fordii*[22]	^{1}H NMR δ (DMSO-d_6): 3.93 (s, 2 × OMe), 3.98 (s, OMe), 5.02 (d, *J* = 7 Hz, H-7'), 6.13 (d, *J* = 9.5 Hz, H-3), 6.66 (s, H-8), 6.72 (s, H-2', H-6'), 7.92 (d, *J* = 9.5 Hz, H-4)
Synthetic	^{1}H NMR δ ($CDCl_3$): 2.07 (s, OAc), 2.36 (s, OAc); ^{13}C NMR δ ($CDCl_3$): 112-32 (C-3), 137.64 (C-4), 139.50 (C-5), 128.90 (C-6), 152.3 (C-7), 93.33 (C-8), 149.6 (C-9), 103.3 (C-10), 133.0 (C-1'), 104 (C-2', C-6'), 152.74 (C-3', C-5'), 129.10 (C-4'), 77.40 (C-7'), 75.23 (C-8'), 62.59 (C-9'), 161.21 (CO)

8 *Daphne oleoide*[23]	^{1}H NMR δ (DMSO-d_6): 7.90 (d, J = 9.5 Hz, H-4), 7.30 (d, J = 8.6 Hz, H-5), 7.06 (d, J = 8.5 Hz, H-6), 6.92 (s, H-2″, H-6″), 6.35 (d, J = 9.5 Hz, H-3), 5.24 (d, J = 2.4 Hz, H-1‴), 5.12 (d, J = 7.4 Hz, H-1′), 4.65 (m, H-2′), 4.15 (m, H-3′), 3.82 (s, 2 × OMe); ^{13}C NMR δ (DMSO-d_6): 160.3 (C-2), 113.5 (C-3), 144.4 (C-4), 119.6 (C-5), 113.1 (C-6), 147.4 (C-7), 138.9 (C-8), 149.4 (C-9), 113.7 (C-10), 77.4 (C-1′), 79.6 (C-2′), 60.9 (C-3′), 127.1 (C-1″), 105.8 (C-2″, C-6″), 150.1 (C-3″, C-5″) 133.8 (C-4″), 100.4 (C-1‴), 72.8 (C-2‴), 74.0 (C-3‴), 70.8 (C-4‴), 72.5 (C-5‴), 61.8 (C-6‴), 56.2 (2 × OMe)
Synthetic	^{1}H NMR δ (DMSO-d_6): 2.27 (s, 3CO OMe), 2.24 (s, 2 × OAc); ^{13}C NMR δ (DMSO-d_6): 170.5, 170.3, 170.2, 169.2, 168.8 (5 × OAc), 20.8, 20.6, 20.4, 20.3, 20.2 (5 × OAc)
9 *Mallotus apelta*[25]	^{1}H NMR δ (DMSO-d_6): 3.68 (br, H-9′), 3.76 (s, MeO-3′), 3.79 (s, MeO-6), 4.24 (m, H-8′), 4.93 (d, J = 7.8 Hz, H-7′), 6.35 (d, J = 9.6 Hz, H-3), 6.53 (s, H-6′), 6.58 (s, H-2′), 6.92 (s, H-5), 7.98 (d, J = 9.6 Hz, H-4), 8.48 (s, HO-4), 9.06 (s, HO-5); ^{13}C NMR δ (DMSO-d_6): 160.05 (C-2), 113.22 (C-3), 144.85 (C-4), 100.86 (C-5), 145.30 (C-6), 137.06 (C-7), 131.64 (C-8), 138.06 (C-9), 111.26 (C-10), 125.87 (C-1′), 103.49 (C-2′), 148.37 (C-3′), 145.75 (C-4′), 134.83 (C-5′), 108.75 (C-6′), 76.35 (C-7′), 77.95 (C-8′), 59.88 (C-9′), 56.01 (OMe-6), 55.88 (OMe-3′)
10 *Duranta repens*[26]	^{1}H NMR δ ($CDCl_3$): 1.86 (s, OAc), 3.53 (dd, J = 12.6, 2.8 Hz, H-9′b), 3.80 (dd, J = 12.6, 1.9 Hz, H-9′a), 3.86 (s, OMe-6), 3.87 (s, OMe-3′), 4.18 (ddd, J = 8.0, 2.8, 1.9 Hz, H-8′), 5.04 (d, J = 8.0 Hz, H-7′), 6.31 (d, J = 9.5 Hz, H-3), 6.82 (s, H-5), 6.85 (d, J = 8.1 Hz, H-5′), 6.94 (dd, J = 8.1, 1.9 Hz, H-6′), 7.05 (d, J = 1.9 Hz, H-2′), 7.86 (d, J = 9.5 Hz, H-4), 8.55 (s, HO-4′); ^{13}C NMR δ ($CDCl_3$): 160.1 (C-2), 114.2 (C-3), 144.0 (C-4), 100.7 (C-5), 145.7 (C-6), 137.1 (C-7), 132.0 (C-8), 140.1 (C-9), 111.9 (C-10), 130.9 (C-1′) 111.9 (C-2′), 151.1 (C-3′) 148.6 (C-4′) 116.3 (C-5′) 121.8 (C-6′) 77.3 (C-7′), 76.6 (C-8′) 62.5 (C-9′) 176.2 (OCOMe), 23.2 (OCOMe), 56.4 (MeO-6), 56.8 (MeO-3′)
11 *Duranta repens*[26]	^{1}H NMR δ ($CDCl_3$: MeOH): 1.87 (s, OC OMe), 3.54 (dd, J = 12.6, 2.6 Hz, H-9′b), 3.83 (dd, J = 12.6, 1.8 Hz, H-9′a), 3.85 (s, OMe-6), 3.88 (s, OMe-3′), 3.90 (s, OMe-4′), 4.18 (ddd, J = 8.1, 2.6, 1.8 Hz, H-8′), 5.03 (d, J = 8.1 Hz, H-7′), 6.30 (d, J = 9.5 Hz, H-3), 6.80 (s, H-5), 6.84 (d, J = 8.1 Hz, H-5′), 6.94 (dd, J = 8.1, 1.9 Hz, H-6′), 7.04 (d, J = 1.8 Hz, H-2′), 7.85 (d, J = 9.5 Hz, H-4); ^{13}C NMR δ ($CDCl_3$: CD_3OD): 160.4 (C-2), 113.8 (C-3), 144.3 (C-4), 100.9 (C-5), 145.8 (C-6), 137.5 (C-7), 131.9 (C-8), 139.6 (C-9), 111.5 (C-10), 130.5 (C-1′), 105.9 (C-2′), 150.0 (C-3′), 139.6 (C-4′), 150.0 (C-5′), 105.9 (C-6′), 77.0 (C-7′), 76.5 (C-8′), 62.0 (C-9′), 176.0 (OCOMe), 32.0 (OCOMe), 56.3 (MeO-6), 56.8 (MeO-3′), 56.8 (MeO-5′)
12 *Duranta repens*[26]	^{1}H NMR δ ($CDCl_3$: MeOH): 1.87 (s, OC OMe), 3.54 (dd, J = 12.5, 2.7 Hz, H-9′b), 3.82 (dd, J = 12.5, 1.9 Hz, H-9′a), 3.87 (s, OMe-6), 3.88 (s, OMe-3′ and 5′),4.19 (ddd, J = 8.1, 2.7, 1.9 Hz, H-8′), 5.04 (d, J = 8.1 Hz, H-7′), 6.32 (d, J = 9.5 Hz, H-3), 6.77 (s, H-2′, H-6′), 6.82 (s, H-5), 7.87 (d, J = 9.5 Hz, H-4), 8.55 (s, OH-4′); ^{13}C NMR δ ($CDCl_3$: CD_3OD): 160.4 (C-2), 113.8 (C-3), 144.3 (C-4), 100.9 (C-5), 145.8 (C-6), 137.5 (C-7), 131.9 (C-8), 139.6 (C-9), 111.5 (C-10), 130.5 (C-1′), 105.9 (C-2′), 150.0 (C-3′), 139.6 (C-4′), 150.0 (C-5′), 105.9 (C-6′), 77.0 (C-7′), 76.5 (C-8′), 62.0 (C-9′), 176.0 (OCOMe), 32.0 (OCOMe), 56.3 (MeO-6), 56.8 (MeO-3′), 56.8 (MeO-5′)
13 *Rhododendron collettianum*[27]	^{1}H NMR δ (C_5D_5N): 6.38 (d, J = 9.4 Hz, H-3), 7.71 (d, J = 9.4 Hz, H-4), 6.72 (s, H-5),7.41 (d, J = 1.9 Hz, H-2′), 7.27 (d, J = 8.1 Hz, H-5′), 7.35 (dd, J = 8.1, 1.9 Hz, H-6′), 5.55 (d, J = 8.0 Hz, H-7′), 4.51 (dt, J = 7.8 Hz, H-8′), 4.26 (br d, J = 12.5 Hz, H-9′), 3.68 (s, OMe), 3.80 (s, OMe); ^{13}C NMR δ (C_5D_5N): 161.5 (C-2), 114.1 (C-3), 144.5 (C-4), 101.5 (C-5), 146.5 (C-6), 139.0 (C-7), 132.7 (C-8), 139.6 (C-9), 112.5 (C-10), 127.2 (C-1′), 113.0 (C-2′), 149.3 (C-3′), 148.1 (C-4′), 117.3 (C-5′), 122.1 (C-6′), 77.5 (C-7′), 80.5 (C-8′), 61.5 (C-9′), 56.0 (OMe-6), 56.1 (OMe-3′)
14 *Antidesma pentandrum*[28]	^{1}H NMR δ ($CDCl_3$): 7.50 (s, H-4), 6.51 (s, H-5), 6.12 (dd, J = 17.4, 10.6 Hz, H-10), 5.09 (d, J = 17.4 Hz, Ha-11), 5.10 (d, J = 10.6 Hz, Hb-11), 1.49 (s, Me-12), 1.49 (s, Me-13), 6.61 (s, H-2′), 6.61 (s, H-6′), 4.61 (d, J = 7.6 Hz, H-7′), 4.21 (dq, J = 7.6, 6.4 Hz, H-8′), 1.29 (d, J = 6.4 Hz, Me-9′) 3.88 (s, MeO-6) 3.92 (s, MeO-3′), 3.92 (s, MeO-5′), 5.62 (s, OH-4′); ^{13}C NMR δ ($CDCl_3$): 159.5 (C-2), 132.7 (C-3), 138.0 (C-4), 111.9 (C-4a), 99.9 (C-5), 145.6 (C-6), 136.6 (C-7), 131.8 (C-8), 137.9 (C-8a), 40.5 (C-9), 145.5 (C-10), 112.1 (C-11), 26.0 (C-12), 26.0 (C-13), 127.0 (C-1′), 104.5 (C-2′), 147.3 (C-3′), 135.6 (C-4′), 147.3 (C-5′), 104.5 (C-6′), 81.6 (C-7′), 74.3 (C-8′), 17.1 (C-9′), 56.2 (MeO-6), 56.5 (MeO-3′), 56.5 (MeO-5′)
15 *Antidesma pentandrum*[28]	^{1}H NMR δ ($CDCl_3$): 7.49 (s, H-4), 6.47 (s, H-5), 6.19 (dd, J = 17.8, 10.4 Hz, H-10), 5.09 (d, J = 17.8 Hz, Ha-11), 5.10 (d, J = 10.4 Hz, Hb-11), 1.49 (s Me-12), 1.49 (s Me-13), 6.84 (br. s H-2′), 6.87 (br. s, H-5′), 6.87 (br. s, H-6′), 4.94 (d, J = 6.3 Hz, H-7′), 4.06 (d, J = 6.3 Hz, H-8′), 5.78 (dd, J = 17.8, 10.4 Hz, H-10), 4.87 (d, J = 17.8 Hz, Ha-11), 4.88 (d, J = 10.4 Hz, Hb-11), 0.96 (s Me-12′), 1.19 (s Me-13′), 3.84 (s, OMe-6), 3.86 (s, OMe-3′), 5.72 (s, OH-4′); ^{13}C NMR δ ($CDCl_3$): 159.7 (C-2), 132.6 (C-3), 138.1 (C-4), 111.9 (C-4a), 99.8 (C-5), 145.4 (C-6), 136.0 (C-7), 132.0 (C-8), 137.9 (C-8a), 40.5 (C-9), 145.6 (C-10), 112.1 (C-11), 26.0 (C-12), 26.0 (C-13), 128.8 (C-1′), 110.9 (C-2′), 146.6 (C-3′), 146.5 (C-4′), 114.4 (C-5′), 121.8 (C-6′), 77.3 (C-7′), 82.6 (C-8′), 40.9 (C-9′), 142.7 (C-10′), 112.7 (C-11′), 25.1 (C-12′), 23.1 (C-13′), 56.0 (MeO-6), 56.3 (MeO-3′)
16 *Antidesma pentandrum*[28]	^{1}H NMR δ ($CDCl_3$): 7.46 (s H-4), 6.50 (s H-5), 6.17 (dd, J = 17.8, 10.2 Hz, H-10), 5.05 (d, J = 17.8 hz, Ha-11), 5.07 (d, J = 10.2 Hz, Hb-11), 1.45 (s Me-12), 1.45 (s Me-13), 6.86 (s, H-2′), 6.86 (s H-5′), 6.86 (s, H-6′), 4.99 (d, J = 5.6 Hz, H-7′), 4.15 (d, J = 5.6 Hz, H-8′), 5.66 (dd, J = 17.8, 10.4 Hz, H-10′), 4.91 (d, J = 17.8 Hz, H-11′), 4.92 (d, J = 10.4 Hz, H-11′), 0.99 (s, Me-12′), 1.17 (s, Me-13′), 3.86 (s, OMe-6), 3.76 (s, OMe-3′), 5.71 (s, OH-4′); ^{13}C NMR δ ($CDCl_3$): 159.7 (C-2), 132.5 (C-3), 138.2 (C-4), 111.7 (C-4a), 101.2 (C-5), 145.6 (C-6), 136.9 (C-7), 131.6 (C-8), 138.3 (C-8a), 40.6 (C-9), 45.8 (C-10), 112.2 (C-11), 26.2 (C-12), 26.2 (C-13), 129.2 (C-1′), 111.0 (C-2′), 146.5 (C-3′), 146.8 (C-4′), 114.4 (C-5′), 121.7 (C-6′), 76.2 (C-7′), 83.0 (C-8′), 41.3 (C-9′), 143.1 (C-10′), 113.1 (C-11′), 25.2 (C-12′), 23.2 (C-13′), 56.9 (MeO-6), 56.2 (MeO-3′)
17 *Antidesma pentandrum*[28]	^{1}H NMR δ ($CDCl_3$): 7.47 (s H-4), 6.46 (s H-5), 6.18 (dd, J = 17.5, 11.0 Hz, H-10), 5.09 (d, J = 17.5 Hz, Ha-11), 5.09 (d, J = 11.0 Hz, Hb-11), 1.49 (s Me-12), 1.49 (s Me-13), 6.75-6.85 (m, H-2′), 6.75-6.85 (m, H-5′), 6.75-6.85 (m, H-6′), 4.93 (d, J = 5.6 Hz, H-7′), 4.02 (d, J = 5.6 Hz, H-8′), 5.76 (dd, J = 17.2, 11.0 Hz, H-10′), 4.87 (d, J = 11.0 Hz, Ha-11′), 4.88 (d, J = 17.2 Hz, Hb-11′), 0.96 (s, Me-12′), 1.15 (s, Me-13′), 3.84 (s, OMe-6)
18 *Protium unifoliolatum*[29]	^{1}H NMR δ ($CDCl_3$): 6.28 (d, J = 9.65 Hz, H-3), 7.96 (d, J = 9.65 Hz, H-4), 3.96 (s, H-11), 3.89 (s, H-11), 3.93 (s, H-13), 6.86 (d, J = 2.12 Hz, H-2′), 6.98 (d, J = 8.12 Hz, H-5′), 6.91 (dd, J = 8.12, 2.12 Hz, H-6′), 4.69 (d, J = 8.01 Hz, H-7′), 4.15 (dd, J = 8.01, 6.36 Hz, H-8′), 1.29 (d, J = 6.36 Hz, Me-9′); ^{13}C NMR δ ($CDCl_3$): 160.57 (C-2), 113.08 (C-3), 138.93 (C-4), 142.19 (C-5), 137.87 (C-6), 141.96 (C-7), 128.58 (C-8), 139.33 (C-9), 107.00 (C-10), 62.25 (C-11),

19 *Mallotus apelta*[30]	^{1}H NMR δ (DMSO-d_6): 6.26 (d, *J* = 9.5 Hz, H-3), 7.90 (d, *J* = 9.5 Hz, H-4), 6.65 (s, H-5), 6.53 (d, *J* = 2.0 Hz, H-2′), 6.58 (d, *J* = 2.0 Hz, H-6′), 4.91 (d, *J* = 8.0 Hz, H-7′), 4.19-4.22 (m, H-8′), 3.39 (dd, *J* = 12.5, 4.5 Hz, H-9′), 3.65 (dd, *J* = 12.5, 2.0 Hz, H-9′), 9.58 (s, OH-6), 9.00 (s, OH-3′), 8.44 (s, OH-4′), 3.75 (OMe-5′); ^{13}C NMR δ (DMSO-d_6): 160.1 (C-2), 113.0 (C-3), 143.0 (C-4), 103.9 (C-5), 144.8 (C-6), 136.6 (C-7), 131.7 (C-8), 136.8 (C-9), 111.5 (C-10), 126.0 (C-1′), 108.7 (C-2′), 145.7 (C-3′), 134.7 (C-4′), 148.3 (C-5′), 103.4 (C-6′), 76.2 (C-7′), 77.9 (C-8′), 59.8 (C-9′), 55.9 (OMe-5′)
20 *Mallotus apelta*[30]	^{1}H NMR δ (DMSO-d_6): 6.25 (d, *J* = 9.5 Hz, H-3), 7.89 (d, *J* = 9.5 Hz, H-4), 6.68 (s, H-5), 6.53 (d, *J* = 2.0 Hz, H-2′), 6.58 (d, *J* = 2.0 Hz, H-6′), 4.87 (d, *J* = 8.0 Hz, H-7′), 4.21-4.25 (m, H-8′), 3.42 (dd, *J* = 12, 5 Hz, H-9′), 3.54 (dd, *J* = 12.0, 3.5 Hz, H-9′), 9.49 (s, OH-6), 9.02 (s, OH-3′), 8.46 (s, OH-4′), 3.76 (OMe-5′); ^{13}C NMR δ (DMSO-d_6): 160.0 (C-2), 113.0 (C-3), 142.9 (C-4), 104.0 (C-5), 144.7 (C-6), 136.1 (C-7), 131.9 (C-8), 136.7 (C-9), 111.4 (C-10), 125.8 (C-1′), 108.7 (C-2′), 145.7 (C-3′), 134.8 (C-4′), 148.4 (C-5′), 103.3 (C-6′), 75.9 (C-7′), 78.2 (C-8′), 60.1 (C-9′), 55.9 (OMe-5′)
21 *Mallotus apelta*[30]	^{1}H NMR δ (DMSO-d_6): 6.30 (d, *J* = 9.5 Hz, H-3), 7.94 (d, *J* = 9.5 Hz, H-4), 6.92 (s, H-5), 6.54 (d, *J* = 1.5 Hz, H-2′),6.59 (d, *J* = 1.5 Hz, H-6′), 4.90 (d, *J* = 8.0 Hz, H-7′), 4.21- 4.24 (m, H-8′), 3.37 (dd, *J* = 12.5, 4.0 Hz, H-9′), 3.62 (dd, *J* = 12.5, 1.5 Hz, H-9′), 3.83 (s, OMe-6) 9.02 (s, OH-3′), 8.46 (s, OH-4′), 3.76 (OMe-5′); ^{13}C NMR δ (DMSO-d_6): 159.9 (C-2), 113.1 (C-3), 144.8 (C-4), 100.9 (C-5), 145.2 (C-6), 138.0 (C-7), 131.8 (C-8), 136.8 (C-9), 111.1 (C-10), 125.8 (C-1′), 108.7 (C-2′), 145.7 (C-3′), 134.8 (C-4′), 148.3 (C-5′), 103.3 (C-6′), 75.9 (C-7′), 78.3 (C-8′), 59.8 (C-9′), 55.9 (OMe-6), 55.8 (OMe-5′)
22 *Eurycorymbus cavaleriei*[32]	^{1}H NMR δ (DMSO-d_6): 6.31 (d, *J* = 9.5 Hz, H-3), 7.94 (d, *J* = 9.5 Hz, H-4), 6.93 (s, H-5), 6.59 (d, *J* = 1.5 Hz, H-2′), 6.54 (d, *J* = 1.5 Hz, H-6′), 4.90 (d, *J* = 7.5 Hz, H-7′), 4.23 (m, H-8′), 3.62 (d, *J* = 12.0 Hz, H-9′), 3.83 (s, OMe-6), 3.76 (s, OMe-3′); ^{13}C NMR δ (DMSO-d_6): 160.0 (C-2), 113.2 (C-3), 144.9 (C-4), 100.9 (C-5), 145.3 (C-6), 136.8 (C-7), 131.9 (C-8), 138.1 (C-9), 111.1 (C-10), 125.8 (C-1′), 103.3 (C-2′), 148.4 (C-3′), 134.8 (C-4′), 145.8 (C-5′), 108.8 (C-6′), 76.0 (C-7′), 78.4 (C-8′), 59.9 (C-9′), 55.8 (OMe-6), 56.0 (OMe-3′)
23 *Duranta repens* L[33]	^{1}H NMR δ ($CDCl_3$): 6.33 (d, *J* = 9.5 Hz, H-3), 7.81 (d, *J* = 9.5 Hz, H-4), 6.78 (s, H-5), 7.10 (d, *J* = 1.9 Hz, H-2′), 6.83 (d, *J* = 8.0 Hz, H-5′), 6.97 (dd, *J* = 8.0, 1.9 Hz, H-6′), 5.09 (d, *J* = 8.1 Hz, H-7′), 4.21 (ddd, *J* = 8.1, 2.5, 1.7 Hz, H-8′), 3.90 (dd, *J* = 12.5, 2.5 Hz, H-9′), 4.13 (dd, *J* = 12.5, 1.7 Hz, H-9′), 6.41 (d, *J* = 15.9 Hz, H-2″), 7.51 (d, *J* = 15.9 Hz, H-3″), 7.40 (d, *J* = 8.0 Hz, H-5″), 6.89 (d, *J* = 8.0 Hz, H-6″), 6.89 (d, *J* = 8.0 Hz, H8″), 7.40 (d, *J* = 8.0 Hz, H-9″), 3.83 (s, OMe-6), 3.89 (s, OMe-3′); ^{13}C NMR δ ($CDCl_3$): 160.5 (C-2), 114.7 (C-3), 144.3 (C-4), 100.6 (C-5), 137.1 (C-6), 132.2 (C-7), 140.8 (C-8), 146.0 (C-9), 112.0 (C-10), 130.9 (C-1′), 111.7 (C-2′), 149.8 (C-3′), 148.5 (C-4′), 116.5 (C-5′), 121.9 (C-6′), 76.9 (C-7′), 75.8 (C-8′), 62.5 (C-9′), 165.7 (C-1″), 117.0 (C-2″), 144.7 (C-3″), 125.9 (C-4″), 130.2 (C-5″), 116.0 (C-6″), 159.3 (C-7″), 116.0 (C-8″), 130.2 (C-9″), 56.4 (OMe-6), 56.0 (OMe-3′)
24 *Duranta repens* L[33]	^{1}H NMR δ ($CDCl_3$): 6.31 (d, *J* 9.5 Hz, H-3), 7.83 (d, *J* = 9.5 Hz, H-4), 6.80 (s, H-5), 7.07 (d, *J* = 1.8 Hz, H-2′), 6.84 (d, 8.2 Hz, H-5′), 6.95 (dd, *J* = 8.2, 1.8 Hz, H-6′), 5.07 (d, *J* = 8.1 Hz, H-7′), 4.20 (ddd, *J* = 8.1, 2.6, 1.7 Hz, H-8′), 3.90 (dd, *J* = 12.6, 2.6 Hz, H-9′), 4.10 (dd, *J* = 12.6, 1.7 Hz, H-9′), 6.45 (d, *J* = 16.0 Hz, H-2″), 7.55 (d, *J* = 16.0 Hz, H-3″), 7.10 (d, *J* = 2.1 Hz, H-5″), 6.70 (d, *J* = 8.0 Hz, H-8″), 7.02 (dd, *J* = 8.0, 2.1 Hz, H-9″), 3.80 (s, OMe-6), 3.85 (s, OMe-3′), 3.77 (s, OMe-6′); ^{13}C NMR δ ($CDCl_3$): 160.3 (C-2), 114.2 (C-3), 144.0 (C-4), 100.8 (C-5), 137.3 (C-6), 132.5 (C-7), 140.9 (C-8), 146.3 (C-9), 111.8 (C-10), 130.6 (C-1′), 111.8 (C-2′), 149.9 (C-3′), 148.7 (C-4′), 116.3 (C-5′), 121.7 (C-6′), 77.2 (C-7′), 76.1 (C-8′), 62.3 (C-9′), 165.5 (C-1″), 117.3 (C-2″), 144.9 (C-3″), 126.4 (C-4″), 112.9 (C-5″), 148.2 (C-6″), 150.3 (C-7″), 116.0 (C-8″), 124.1 (C-9″), 56.3 (OMe-6), 55.9 (OMe-3′), 56.1 (OMe-6″)
25 *Duranta repens* L[33]	^{1}H NMR δ ($CDCl_3$): 6.30 (d, *J* = 9.5 Hz, H-3), 7.85 (d, *J* = 9.5 Hz, H-4), 6.80 (s, H-5), 7.05 (d, *J* = 1.9 Hz, H-2′), 6.81 (d, *J* = 8.1 Hz, H-5′), 6.94 (dd, *J* = 8.1, 1.9 Hz, H-6′), 5.06 (d, *J* = 8.1 Hz, H-7′), 4.19 (ddd, *J* = 8.1, 2.7, 1.9 Hz, H-8′), 3.89 (dd, *J* = 12.6, 2.7 Hz, H-9′), 4.15 (dd, *J* = 12.6, 1.9 Hz, H-9′), 6.38 (d, *J* = 16.2 Hz, H-2″), 7.47 (d, *J* = 16.2 Hz, H-3″), 7.08 (d, *J* = 2.2 Hz, H-5″), 6.90 (d, *J* = 8.0 Hz, H-8″), 6.95 (dd, *J* = 8.0, 2.2 Hz, H-9″), 3.81 (s, OMe-6), 3.86 (s, OMe-3′); ^{13}C NMR δ ($CDCl_3$): 160.4 (C-2), 113.9 (C-3), 144.2 (C-4), 100.6 (C-5), 137.0 (C-6), 132.3 (C-7), 140.7 (C-8), 146.2 (C-9), 111.9 (C-10), 130.7 (C-1′), 111.7 (C-2′), 149.7 (C-3′), 148.4 (C-4′), 116.1 (C-5′), 121.8 (C-6′), 77.3 (C-7′), 76.0 (C-8′), 62.4 (C-9′), 165.3 (C-1″), 117.5 (C-2″), 144.8 (C-3″), 126.3 (C-4″), 113.5 (C-5″), 144.7 (C-6″), 147.3 (C-7″), 116.0 (C-8″), 123.9 (C-9″), 56.5 (OMe-6), 56.0 (OMe-3′)
26 *Duranta repens* L[33]	^{1}H NMR δ ($CDCl_3$): 6.32 (d, *J* = 9.5 Hz, H-3), 7.83 (d, *J* = 9.5 Hz, H-4), 6.79 (s, H-5), 6.89 (s, H-2′), 6.89 (s, H-6′), 5.03 (d, *J* = 8.1 Hz, H-7′), 4.05 (ddd, *J* = 8.1, 2.6, 1.8 Hz, H-8′), 3.93 (dd, *J* = 12.5, 1.8 Hz, H-9′), 4.13 (dd, *J* = 12.5, 2.6 Hz, H-9′),7.50 (d, *J* = 2.0 Hz, H-3″), 6.96 (d, *J* = 8.3 Hz, H-6″), 7.46 (dd, *J* = 8.3, 2.0 Hz, H-7″), 3.79 (s, OMe-6), 3.85 (s, OMe-3′), 3.85 (s, OMe-5′); ^{13}C NMR δ ($CDCl_3$): 160.2 (C-2), 114.4 (C-3), 144.0 (C-4), 100.5 (C-5), 137.3 (C-6), 132.4 (C-7), 140.6 (C-8), 146.3 (C-9), 112.0 (C-10), 130.6 (C-1′), 111.63 (C-2′), 149.9 (C-3′), 148.6 (C-4′), 116.4 (C-5′), 122.3 (C-6′), 77.0 (C-7′), 75.9 (C-8′), 62.7 (C-9′), 163.0 (C-1″), 124.2 (C-2″), 115.7 (C-3″), 144.1 (C-4″), 145.6 (C-5″), 116.2 (C-6″), 127.9 (C-7″), 56.2 (OMe-6), 56.6 (OMe-3′), 56.6 (OMe-5′)
27 *Jatropha gossypifolia*[24]	^{1}H NMR δ ($CDCl_3$): 4.42-4.28, (m, H-9′); Remaining data is same as **1;** ^{13}C NMR δ ($CDCl_3$): 62.75 (C-9′); Remaining data is same as **1**
28 *Cleome viscose*[20]	^{1}H NMR δ (DMSO-d_6): 6.32 (d, *J* = 9.4 Hz, H-3), 7.96 (d, *J* = 9.4 Hz, H-4), 6.95 (s, H-5), 6.77 (s, H-2′), 6.77 (s, H-6′), 4.96 (d, *J* = 8.1 Hz, H-7′), 4.37 (m, H-8′), 3.39 (dd, *J* = 4.4, 12.4 Hz, H-9′), 3.63 (br d, *J* = 12.4 Hz, H-9′), 3.78 (s, 2 × OMe), 3.85 (s, OMe), 5.04 (s, OH), 8.61 (s, OH); ^{13}C NMR δ (C_5D_5N): 160.7 (C-2), 113.7 (C-3), 144.3 (C-4), 101.1 (C-5), 146.2 (C-6), 138.6 (C-7), 133.1 (C-8), 139.4 (C-9), 111.7 (C-10), 126.4 (C-1′), 106.4 (C-2′), 149.3 (C-3′), 149.3 (C-5′), 106.4 (C-6′), 77.4 (C-7′), 80.1 (C-8′), 61.0 (C-9′), 56.3 (2 × OMe), 56.1 (OMe)

Seligmann and coworkers[16] described the isolation of new coumarinolignoid, 2-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxymethyl-2,3-dihydro-1, 4, 5-trioxaphenanthren-6-one, (**4, 29**) known as daphneticin from the roots of *Daphne tangutica*. Cottiglia *et al*.[17] reported the isolation of same compound from the leaves of *Daphne gnidium* L. in 2002, which showed promising biological activity. Some other new coumarinolignoids were also isolated from *Hemidesmus indicus* R. Br. and *Salsola laricifolia1*[8].

Aquillochin also known as cleomiscosin C (**5**) was isolated by Cordell *et al*.[19] from *Aquilaria agallocha*. The complete spectral detail of all three cleomiscosins from *Cleome viscose* L. was discussed by Ray *et al*.[20]. The antihepatotoxic activity of **1**, **3** and **5** was also explored.

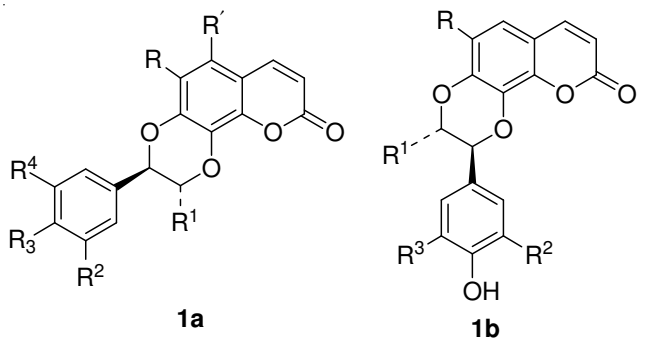


Fig. 2. Regioisomers of coumarinolignoid

TABLE-3
MOIETIES FOR **1a**

Compd. No	R	R^1	R^2	R^3	R^4	R^7
1	OMe	CH_2OH	H	OH	OMe	H
27	OMe	CH_2OAc	H	OH	OMe	H
2	OMe	CH_3	H	OH	OMe	H
4	H	CH_2OH	OMe	OH	OMe	H
5	OMe	CH_2OH	OMe	OH	OMe	H
9	OMe	CH_2OH	OMe	OH	H	H
10	OMe	CH_2OAc	OMe	OH	H	H
11	OMe	CH_2OAc	OMe	OMe	H	H
12	OMe	CH_2OAc	OMe	OH	OMe	H
13	OMe	CH_2OH	OMe	OH	H	H
18	OMe	CH_3	H	OH	OMe	OMe
19	OH	CH_2OH	OH	OH	OMe	H

TABLE-4
MOIETIES FOR **1b**

Compd. No	R	R^1	R^2	R^3
3	OMe	CH_2OH	H	OMe
30	OMe	CH_3	H	OMe
29	H	CH_2OH	OMe	OMe
28	OMe	CH_2OH	OMe	OMe
20	OH	CH_2OH	OH	OMe
21	OMe	CH_2OH	OH	OMe
22	OMe	CH_2OH	OMe	OH

Shamsuddin and co-workers[21] described the isolation of new coumarinolignoid, moluccanin (**6, 31**) from the stems of *Aleurrites moluccana* in 1988. In the next year aleuritin (**7**) was isolated by the same research group[22] from the stems of *Aleurites fordii*. After a decade Ahmad *et al.*[23] isolated a new coumarinolignoid glycoside, daphneticin-4''-*O*-α-D-glucopyranoside (**8**) together with known daphneticin from the extract of *Daphne oleoides*. The first natural acylated coumarinolignoids[27] was isolated from *Jatropha gossypifolia* in 1999 by Vankatasin[24].

Cheng and coworkers[25] reported the isolation of a new coumarinolignoid, 5'-demethylaquillochin (**9**) along with two known compounds **1** and **5** from the roots of *Mallotus apelta* (Fig. 3).

Iqbal and coworkers[26] achieved the isolation of three new coumarinolignoids, durantin A-C, (**10**, **11** and **12**) from *Duranta repens*. Moreover, compound **1** was also extracted and characterized from the same plant. These compounds exhibited phosphodiesterase inhibitory activity (Table-6).

Hussain *et al.*[27] explored new coumarinolignoid 8'-epi-cleomiscosin A (**13**) from the aerial parts of *Rhododendron collettianum*. In addition, two known coumarinolignoids **1** and **5** were also reported first time from this plant. Compound **13** has strong inhibitory activity against enzyme tyrosine as compared to the standard tyrosine inhibitiors, making it valuable for the treatment of hyperpigmentation.

Cheng *et al.*[28] described the isolation of four new coumarinolignoids, antidesmanin A-D 7-(1,1-dimethylallyl)-2,3-dihydro-3-(4-hydroxy-3,5-dimethoxyphenyl)-10-methoxy-2-methyl-6*H*-1,4,5-trioxaphenanthren-6-one (**14**), 3,7-*bis*-(1,1-dimethylallyl)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-10-methoxy-6*H*-1,4,5-trioxaphenanthren-6-one (**15**), 2,7-*bis*-(1,1-dimethylallyl)-2,3-dihydro-3-(4-hydroxy-3-methoxyphenyl)-10-methoxy-6*H*-1,4,5-trioxaphenanthren-6-one (**16**), 2-(3,4-dihydroxyphenyl)-3,7-*bis*-(1,1-dimethylallyl)-2,3-dihydroxy-10-methoxy-6*H*-1,4,5-trioxaphenanthren-6-oneor-3-(3,4-dihydroxyphenyl)-2,7-*bis*-(1,1-dimethylallyl)-2,3-dihydro-10-methoxy-6*H*-1,4,5-trioxaphenanthren-6-one (**17**) from the root of *Formosan Antidesma* pentandrum var. barbatum. All compounds except **15** were evaluated as cytotoxic agents.

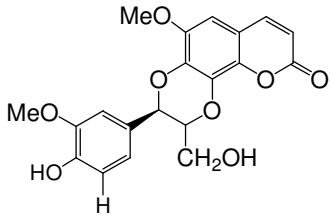
Magalhaes *et al.*[29] isolated the derivative of **2** as 5-methoxy-propacin (**18**) from the wood of *Protium unifoliolatum*. The structure of this novel compound was elucidated by using infrared, 1D, 2D-NMR and mass spectroscopic techniques.

Feng and his colleagues[30] reported three new coumarinolignoids, malloapelin A-C, 3-(3,4-dihydroxy-5-methoxyphenyl)-2,3-dihydro-5-hydroxy-2-(hydroxymethyl)-9*H*-pyrano[2,3-f][1,4]benzodioxin-9-one) as **19**, 2-(3,4-dihydroxy-5-methoxyphenyl)-2,3-dihydro-5-hydroxy-3-(hydroxymethyl)- 9*H*-pyrano[2,3-f][1,4]benzodioxin-9-one) as **20** and 2-(3,4-dihydroxy-5-methoxyphenyl)-2,3-dihydro-3-(hydroxymethyl)-5-methoxy-9*H*-pyrano[2,3-f][1,4]benzodioxin-9-one) as[21], respectively from the roots of *Mallotus apelta*. Three known coumarinolignoids **1**, **3** and **9** were also extracted from this plant. Hence this plant is a rich source of antihepatotoxic agents due to the presence of three pairs of regioisomeric coumarinolignoids.

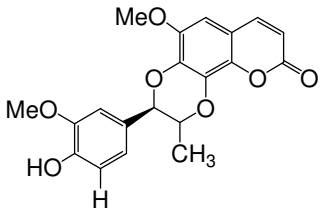
Michalet and coworkers[31] isolated the cleomiscosin A from the bark of *Christiana africana*. Moreover, this plant is a rich source of other natural products like alkaloids, flavonoids and terpenoids. Isolation of new coumarinolignoid, 7',8'-dihydro-7'-(3'-methoxy-4',5'-dihydroxyphenyl)-8'-(hydroxymethyl)-6-methoxy-2*H*-pyrano[2,3-f]-7,8-benzodioxin-2-one) (**22**) commonly called 5'-hydroxycleomiscosin, from the twigs of *Eurycorymbus cavaleriei* was recently described by Zhang *et al.*[32] (Fig. 4). Biological studies showed that **22** has quinone reductase induction activity.

In 2009, Ahmad *et al.*[33] reported four new coumarinolignoids; repenins A-D (**23-26**) alongwith **1** and **10** from the whole plant of *Duranta repens* L. The spectroscopic data established the structure of new compounds. Coumarinolignoids obtained from this source have promising antioxidative scavenging activity.

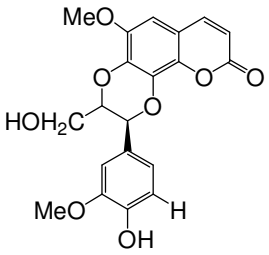
Syntheses: The first synthesis of cleomiscosin A (**1**), B (**3**), C (**5**), propacin (**2, 30**) and daphneticin (**4**) were reported by Cordell and coworkers[19] in 1984 by using chemical and enzymatic oxidation reactions (**Scheme-I**). Different precursors of phenyl propene and coumarin were used to afford isomeric coumarinolignoids at moderate conditions (Table-5).



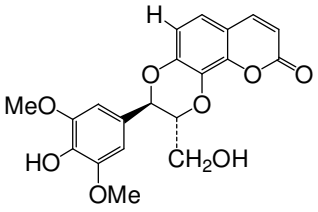
Cleomiscosin A **1**



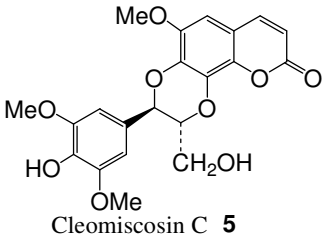
Propacin **2**



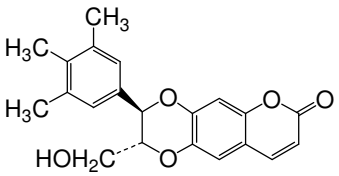
Cleomiscosin B **3**



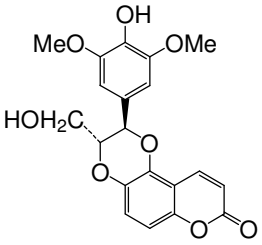
Daphneticin **4**



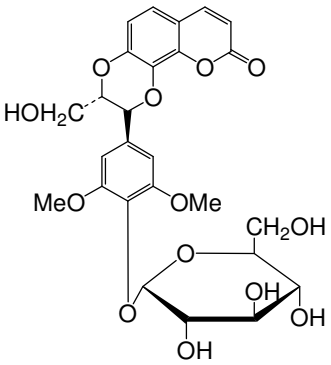
Cleomiscosin C **5**



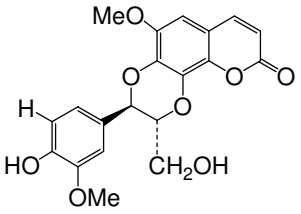
Moluccanin **6**



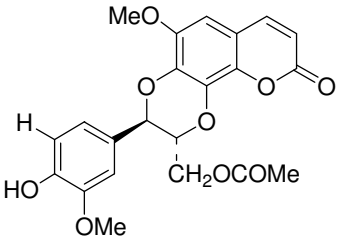
Aleuritin **7**



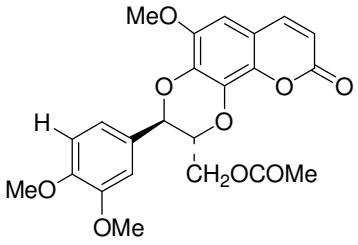
Daphneticin-4"-O-α-D-glucopyranoside **8**



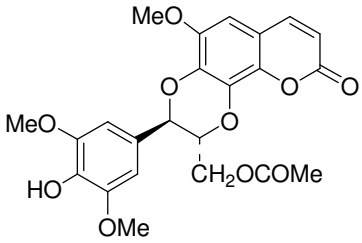
5'-Demethylaquillochin **9**



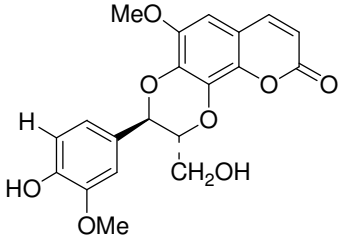
Durantin A **10**



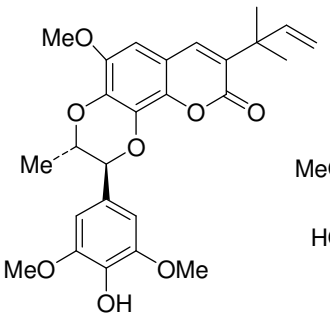
Durantin B **11**



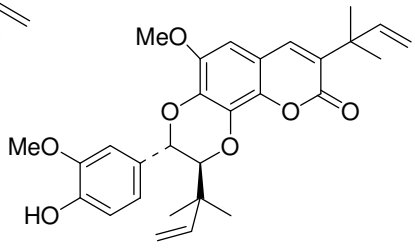
Durantin C **12**



8'-Epi-cleomiscosin A **13**

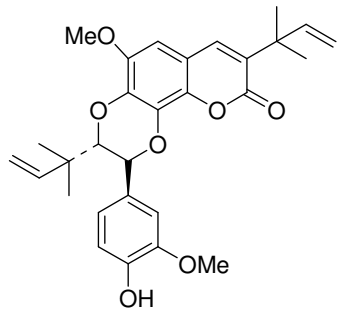


Antidesmanin A **14**

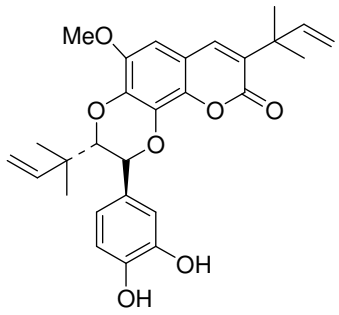


Antidesmanin B **15**

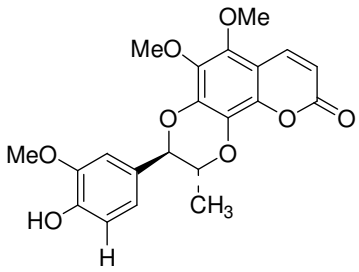
Fig. 3. Structures of some potent coumarinolignoids



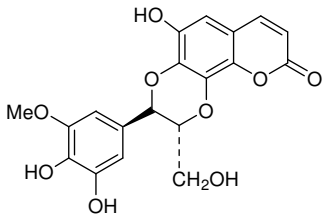
Antidesmanin C **16**



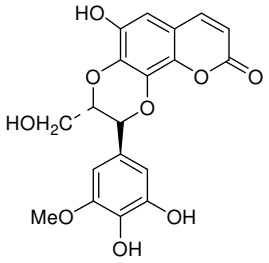
Antidesmanin D **17**



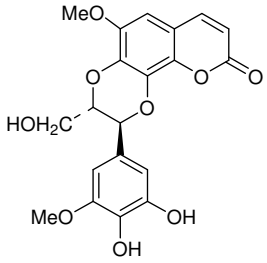
5-Methoxypropacin **18**



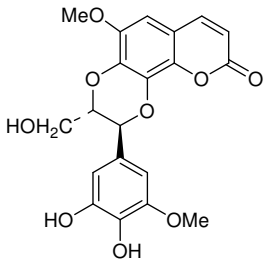
Malloapelin A **19**



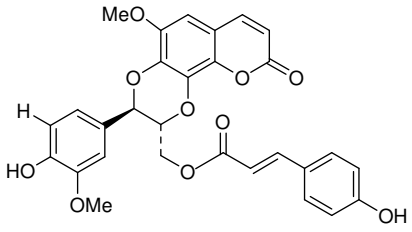
Malloapelin B **20**



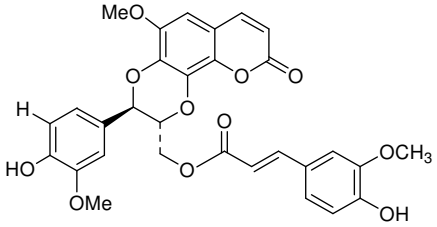
Malloapelin C **21**



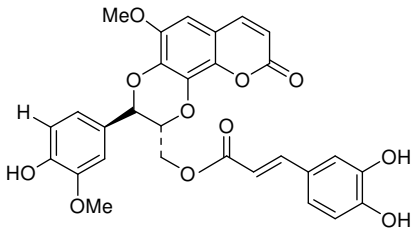
5'-Hydroxycleomiscosin B **22**



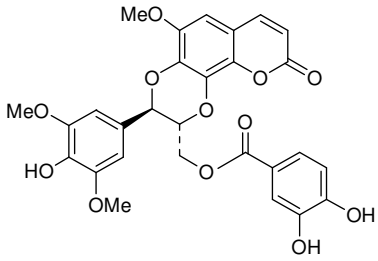
Repenins A **23**



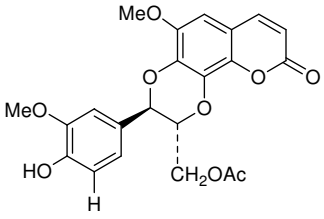
Repenins B **24**



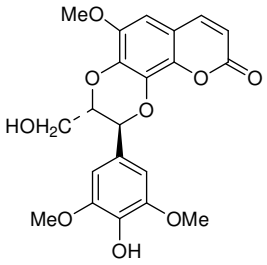
Repenins C **25**



Repenins D **26**

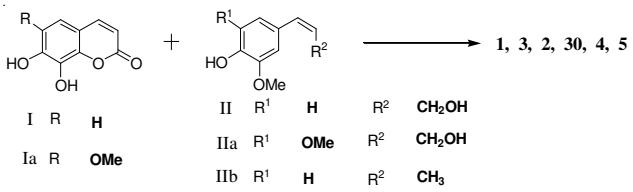


Venkatasin **27**



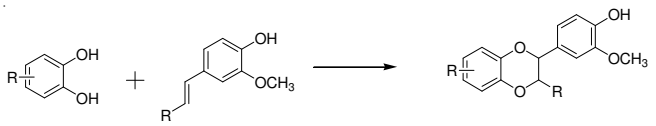
Cleomiscosin D **28**

Fig. 4 Structures of some bioactive coumarinolignoids



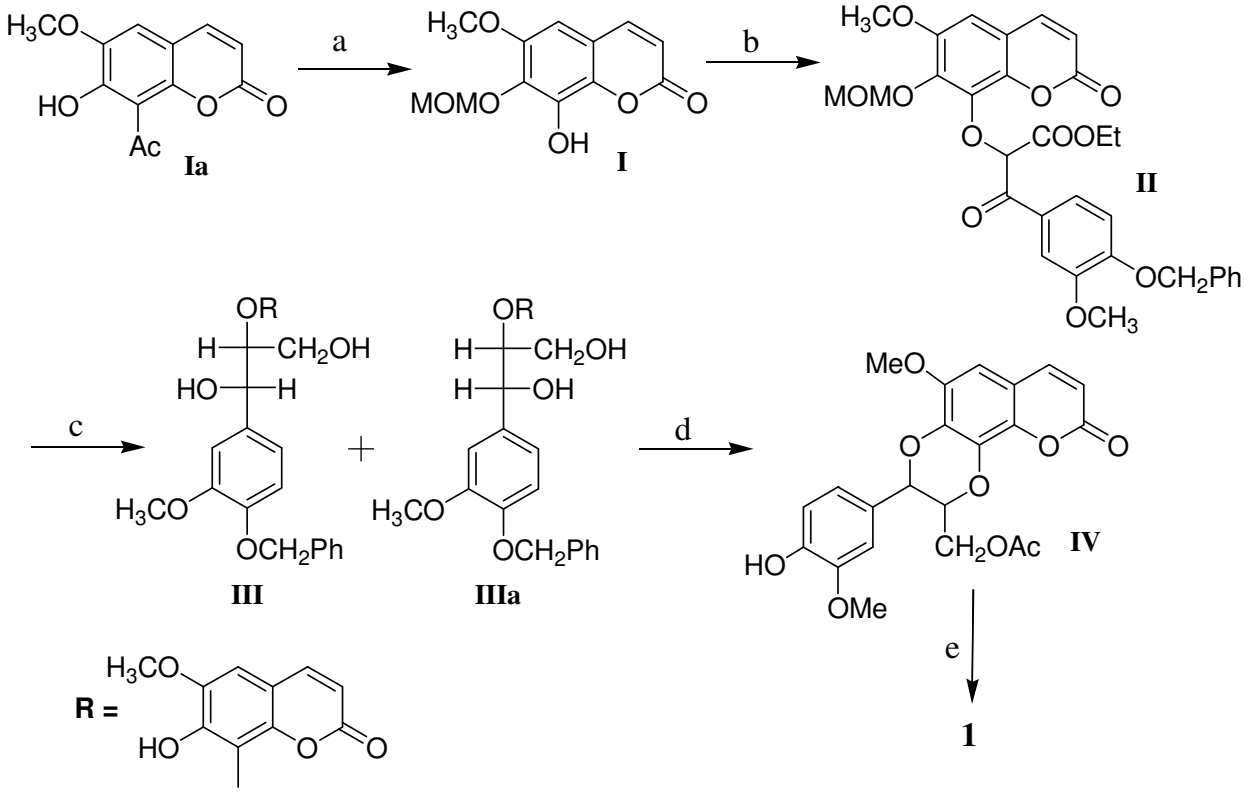
Scheme-I: Cleomiscosin A, B, C, Propacin and Daphneticin

Arnoldi *et al.*[34] reported an efficient synthesis of natural propacin (**2, 30**), cleomiscosin A (**1**) and B (**3**). Equimolar ratio of 7,8-dihydroxy-6-methoxycoumarin and isoeugenol were oxidized with Ag_2O at room temperature to furnish **2** in 30 % yield. Similarly, fraxetin on reaction with coniferyl alcohol afforded the mixture of **1** and **3** (**Scheme-II**).



Scheme-II: Synthesis of Natural Propacin, Cleomiscosin A and B
(The regioisomers were distinguished on the basis of heteronuclear selective decoupling technique)

An effective approach for the large scale synthesis of cleomiscosin A (**1**) from methoxymethyl ether of 8-acetyl-7-



Reagents and conditions: a = (i) NaH, THF, 1 h (ii) CH_3-O-CH_2-Cl, 3 h, (iii) 30 % H_2O_2, NaOH, Dioxane b = (i) t-BuOK, DMF, 1 h, rt (ii) ethyl-2-bromo-3-(4-benzyloxy-3-methoxyphenyl)-3-oxopropionate, DMF, 3 h, rt c = (i) 2N HCl-MeOH, (ii) $LiBH_4$, THF d = CH_3COOH, 5 % H_2SO_4, 60 ºC e = (i) 1 % NaOH at 0 ºC (ii) MeOH

Scheme-III: Total Synthesis of Cleomiscosin A

hydroxy-6-methoxycoumarin **I** was explained by Ito and coworkers[35]. Ketoester II was prepared by the condensation of **I** with ethyl-2-bromo-3-(4-benzyloxy-3-methoxyphenyl)-3-oxopropionate. After the removal of methoxy methyl group from **II**, reduction was achieved by using $LiBH_4$ that afforded erythro isomer predominantly. The mixture of diol was transformed into acetate **IV** by 5 % H_2SO_4 in acetic acid in 50 % yield while subsequent base hydrolysis gave cleomiscosin A (**1**) in 96 % yield (**Scheme-III**).

TABLE-5
SYNTHESIS OF COUMARINOLIGNOIDS BY OXIDATION

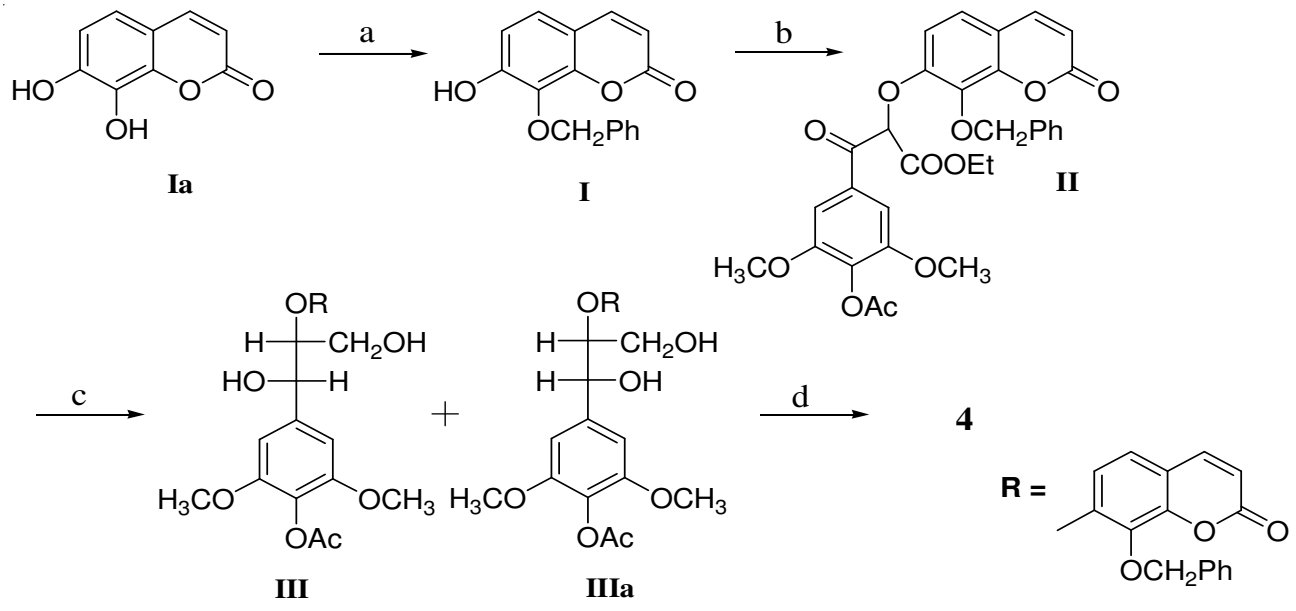
S. No.	Coumarin	Phenylpropene	Reagents, temperature, time	Yield of isomeric coumarinolignoids (%)
1	Ia	II	Ag_2O rt, 20 h	10.4, 6.5 **(1, 3)**
2	Ia	II	HRP 37 ºC, 7days	22.6, 2.7 **(1, 3)**
3	Ia	IIb	Ag_2O rt, 20 h	4.1 **(2 or 30)**
4	Ia	IIb	HRP 37 ºC, 7days	29 **(2 or 30)**
5	Ia	IIb	HRP-H_2O_2 14 days, 37 ºC	87.2 **(2 or 30)**
6	Ia	IIa	Ag_2O rt, 18 h	6.8 **(5)**
7	Ia	IIa	HRP 37 ºC, 14 days	17.5 **(5)**
8	I	IIa	Ag_2O rt, 24 h	1 **(29)**
9	I	IIa	HRP 37 ºC, 19 days	5.8 **(29)**

Cordell *et al.*[36] proposed a unidirectional method for structure determination of natural 1,4-dioxane ring system like **2, 30, 4** and **5**. They used selective INEPT plus program.

Tanaka, Kato and Ito[37] have developed a facile synthesis of daphneticin by adopting the mono-debenzylation strategy of 7,8-dibenzyloxycoumarin in mild conditions. Bromination of ethyl 3-(4-benzyloxy-3,5-dimethoxyphenyl)-3-oxopropionate followed by acetylation furnish ethyl-2-bromo-3-(4-acetoxy-3,5-dimethoxyphenyl)-3-oxopropionate. The monobenzylated product was condensed with prepared bromooxopropionate compound in the presence of NaH followed by $LiBH_4$ reduction to afford mixture of diols. The cyclization achieved in acetic acid and 36 % HCl at 60 ºC to give 68 % yield of exclusive daphneticin (**Scheme-IV**).

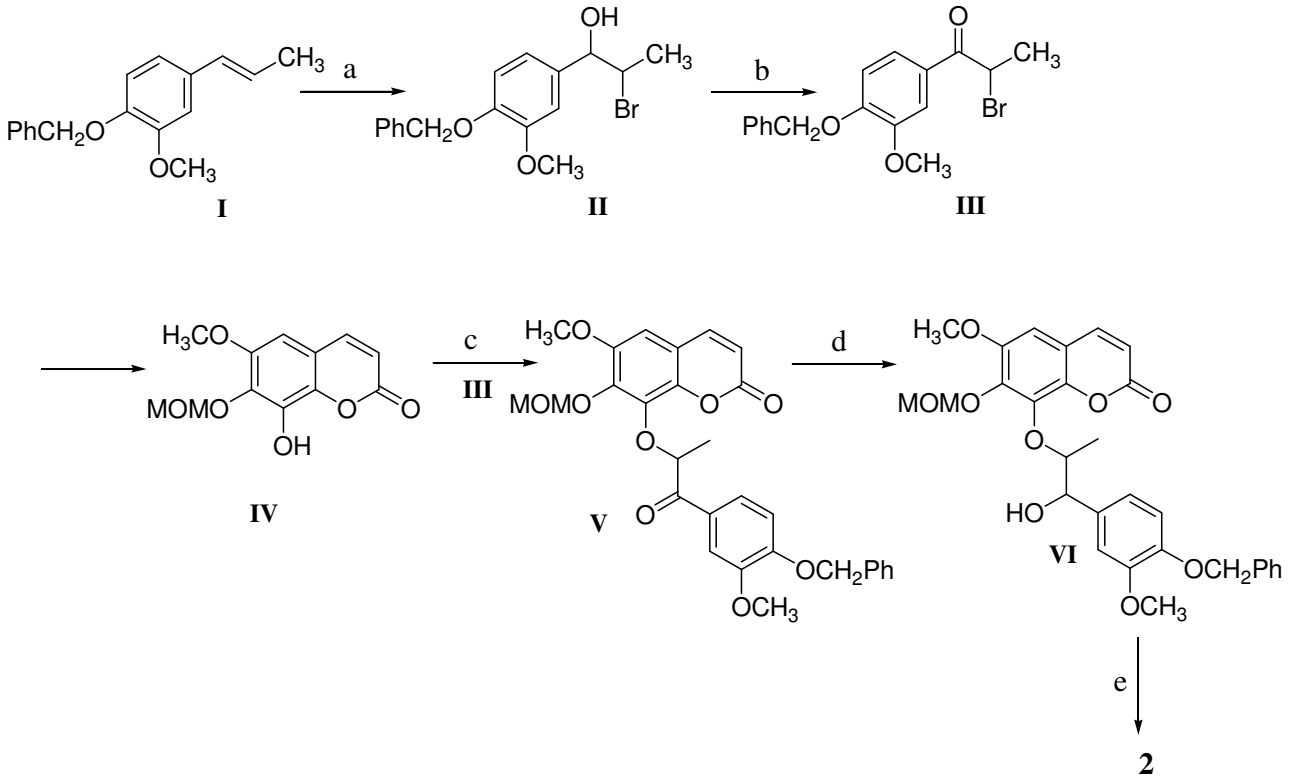
Ichino *et al.*[38] prepared 7-benzyloxy-8-hydroxycoumarin that was oxidized in the presence of hydrogen peroxide in alkaline medium. This compound was converted into methoxymethyl ether followed by reductive debenzylation. 7-Hydroxy-8-methoxymethoxycoumarin after treatment of methansulfonyl chloride followed by benzylation and base hydrolysis afford 8-benzyloxy-7-hydroxycoumarin. The formation of daphneticin (**4**) was similar as adopted in previous paper[37].

The same authors[39] also described the total synthesis of daphneticin and its regioisomers and proposed the total synthesis of propacin **2** and its regioisomer **30**. Isobenzyleugenol **I** transformed into its bromohydrin derivative **II** with the help of bromoacetamide. It was oxidized into 1-(4-benzyloxy-3-methoxy phenyl)-2-bromo-1-propanone **III** and condensed with 7-methoxymethyl fraxetin **IV** in the presence of tBuOK to afford condensed product **V**, which was treated with lithium borohydride and gave corresponding alcohol **VI**. It was cyclized by the action of conc. HCl *via* a quinone methide intermediate to afford propacin **2** (**Scheme-V**).



Reagents and conditions: a = (i) *n*-BuCl, anhyd. K_2CO_3, DMF, 60 ºC, 13 h (ii) TFA, C_6H_6, rt, 5 h, b = (i) Ethyl-3-(4-benzyloxy-3,5-dimethoxyphenyl)-3-oxopropionate, Br_2, $CHCl_3$ (ii) Ac_2O, Py, rt, (iii) NaH, DMF-THF c = (i) $LiBH_4$, dry THF, 0 ºC, d = 36 % HCl, CH_3COOH, 60 ºC

Scheme-IV: Total synthesis of daphneticin



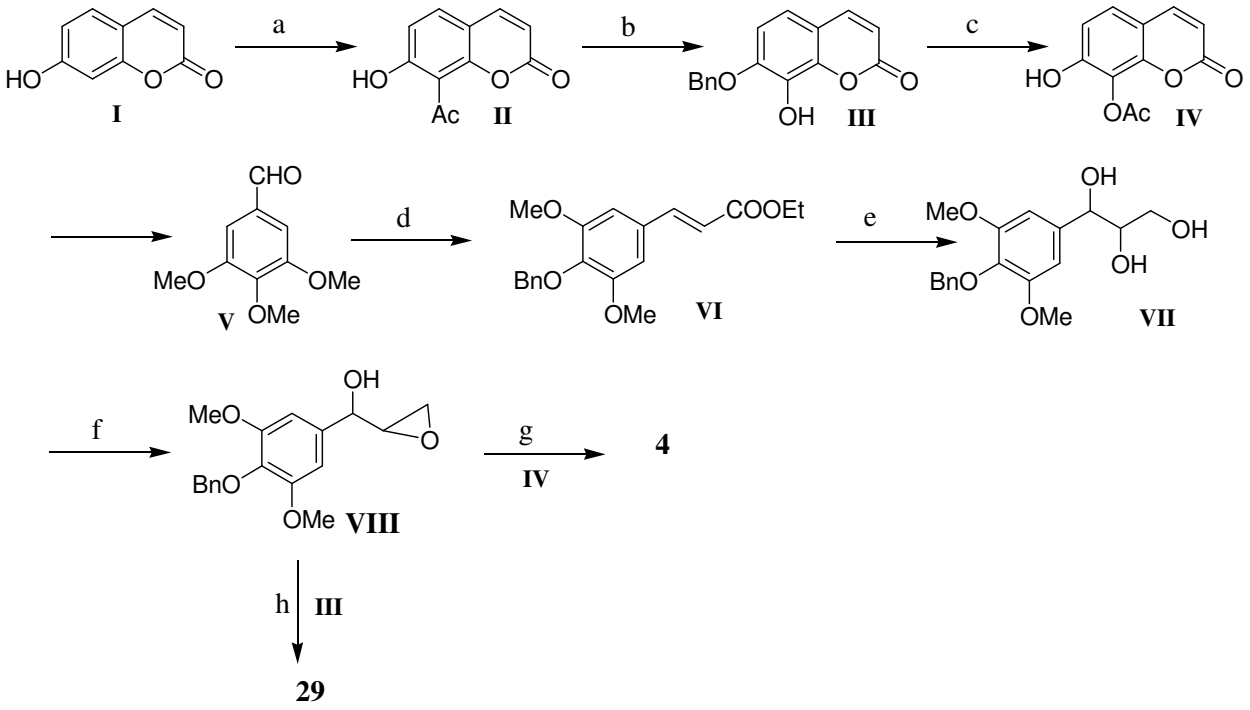
Reagents and conditions: a = (i) $HClO_4$, Dioxane, ice water, *N*-bromoacetamide, 0 ºC, 1 h, (ii) Sod. Dithionate, ice water, Et_2O, b = MnO_2, CH_2Cl_2, 30 min., rt, c = Acetonitrile, t-BuOK, 30 min., rt, d = $LiBH_4$, THF, 0 ºC, 10 min., N_2, e = (i) 35 % HCl, CH_3COOH, 60 ºC, 30 min.

Scheme-V: Total Synthesis of propacin and its regioisomer

The regioisomer of propacin **30** was synthesized by benzylation of 7-methoxymethyl fraxetin **IV** and condensed with **III**. The condensed product was reduced to gave diastereomeric mixture of alcohol, it was separated and cyclized with the help of conc. HCl/AcOH to furnish **30**.

Ichino *et al.*[40] described the total synthesis of cleomiscosin C (aquillochin) **5**, its regioisomers and cleomiscosin D **28** from easily available precursors. Same strategy was adopted in this synthesis as for the total synthesis of cleomiscosin A **1**, daphneticin **4** and propacin **2**, **30**.

Tanaka and coworkers[41] have developed a better way for the synthesis of **1**, **2**, **4** and **5** by the application of diphenyl selenoxide (Ph_2SeO) as oxidizing agent rather Ag_2O/DDQ. Oxidative coupling of 7,8-dihydroxycoumarins took place with



Reagents and conditions: a = (i) Ac_2O, Py, rt, 24 h, 97 % (ii) $AlCl_3$, 160 ºC, 2 h, 97 %, b = (i) BnBr, K_2CO_3, 24 h, 94 % (ii) H_2O_2, NaOH, 20 min., 94 %, c = (i) Ac_2O, Py, rt, 24 h, 90 % (ii) Pd/C (5 %), H_2, EtOAc, rt, 6 h, 92 % d = (i) Piperidine, H_2O, reflux, 48 h, 80 % (ii) CO_2HCH_2CO2Et, Py, Piperidine, reflux, 6 h, (iii) *n*-BuBr, K_2CO_3, 24 h, 80 %, e = (i) LAH, $AlCl_3$, THF, 30 min., 86 % (ii) AD-mix-β, $MeSO_2NH_2$, t-BuOH, H_2O, 0 ºC, 20 h, 87 %, f = (i) TsCl, Py, 91 % (ii) K_2CO_3, MeOH, rt, 3 h, 80 % g = (i) DIAD, Ph_3P, THF, rt, 24 h, 65 % (ii) K_2CO_3, MeOH, rt, 3 h, 90 % (iii) Pd/C (5 %), H_2, EtOAc, rt, 6 h, 81 %, h = (i) DIAD, Ph_3P, THF, rt, 24 h, 65 % (ii) Pd/C (5 %), H_2, EtOAc, rt, 6 h, 81 % (iii) K_2CO_3, MeOH, rt, 3 h, 90 %

Scheme-VI: First Enantioselective synthesis of daphneticin and its regioisomer

TABLE-6
BIOLOGICAL SIGNIFICANCE OF COUMARINOLIGNOIDS

No.	Biological Activities	Coumarinolignoids	Sources	Ref.
1	Antibacterial, Anticancer	Daphneticin	*Daphne gnidium* L. *Daphne tangutica*	18, 44
2	Antihepatotoxic, Modulate humorral and cell mediated immune response	Cleomiscosin A-C	*Cleome viscosa*	8, 20, 43
3	Antioxidant	Repenins A-D, Cleomiscosin A, Durantin A	*Duranta repens* L.	33
4	Antitumor	Cleomiscosin A	*Cleome viscosa*	35
5	Cytotoxic	Antidesmanin A-C, Daphneticin, Cleomiscosin A	*Antidesma pentandrum, Daphne tangutica, Cleome viscose*	28, 17, 8
6	Hepatoprotective	Malloapelin C	*Mallotus apelta*	30
7	Phosphodiesterase inhibitor	Cleomiscosin A, Durantin A-C	*Duranta repens*	26
8	Quinone reductase induction activity	5'-Hydroxycleomiscosin	*Eurycorymbus cavaleriei*	32
9	Tyrosine Inhibitor	8'-Epi-cleomiscosin A	*Rhododendron collettianum*	27

phenylpropenes. This method induced high stereo- and regioselectivity in products. According to the mechanism, the hydroxyl group in 7, 8-dihydroxycoumarins would be oxidized to *o*-quinines in the presence of Ph_2SeO. The oxygen atom at C-8 was readily attacked by double bond of phenylpropenes to furnish natural coumarinolignoids (**1, 2, 4** and **5**).

Pan *et al*.[42] proposed the first enantioselective synthesis of daphneticin **4** and its regioisomers **29** by using convergent strategy. 7-Hydroxycoumarin was converted into 8-acetoxy-7-hydroxycoumarin in the first step. Several other steps produced 2, 3-expoxy-1-(4-benzyloxy-3, 5-dimethoxyphenyl) propanol, that reacted further by Mitsunobu reaction for the inversion of configuration and furnished **4**. Similar approach was adopted for the synthesis of regioisomer **29** by using 7-benzyloxy-8-hydroxycoumarin (**Scheme-VI**). Coumarinolignoids have paramount importance in pharmaceutics due to various biological activities summarized in Table-6.

Conclusion

This review article invites the researchers to explore the diverse method of synthesis other than oxidative coupling related to this rare natural product class. These methods should be environment friendly and more reproducible in outcome. Because of having varied biological activities, its some known and unknown derivatives may grasp the attention of scientists to step forward for new directions.

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REFERENCES

1. A. Chatterjee, P.C. Das, P.C. Joshi and S. Mandal, *J. Indian Chem. Soc.*, **71**, 475 (1994).
2. R. Hansel, J. Schulz and A. Pelter, *Chem. Ber.*, **108**, 1482 (1975).
3. J.F.J. Castelao, O.R. Gottlieb, R.A. de. Lima, A.L. Mesquita, H.E. Gottlieb and E. Wenkert, *Phytochemistry*, **16**, 735 (1977).
4. H. Nielsen and P. Arends, *Phytochemistry*, **17**, 2040 (1978).
5. A.B. Ray, S.K. Chattopadhyay, C. Konno and H. Hikino, *Tetrahedron Lett.*, **21**, 4477 (1980).
6. A.B. Ray and S.K. Chattopadhyay, *Heterocycles*, **19**, 19 (1982).
7. R. Vanhaelen-Fastre, L. Luyengi, M. Vanhaelen, J.P. Declercq and M.V. Meerssche, *Phytochemistry*, **26**, 317 (1987).
8. H. Tanaka, I. Kato, K. Ichino and K. Ito, *J. Nat. Prod.*, **49**, 366 (1986).
9. M. Arisawa, S.S. Handa, D.D. Mcpherson, D.C. Lankin, G.A. Cordell, H.H.S. Fong and N.R. Farnsworth, *J. Nat. Prod.*, **47**, 300 (1984).
10. M. Mizuno, H. Kojima, T. Tanaka, M. Iinuma, R. Kimura, M. Zhi-da and H. Murata, *Phytochemistry*, **26**, 2071 (1987).
11. E.X. Almeida, L.M. Conserva and R.P.L. Lemos, *Biochem. Sys. Ecol.*, **30**, 685 (2002).
12. B. Das, A. Kashinatham, B. Venkataiah, K.V.N.S. Srinivas, G. Mahender and M.R. Reddy, *Biochem. Sys. Ecol.*, **31**, 1189 (2003).
13. M.D.G.B. Zoghbi, N.F. Roque and O.R. Gottlieb, *Phytochemistry*, **20**, 180 (1981).
14. M.R. Parthasarathy and K.P. Saradhi, *Phytochemistry*, **23**, 867 (1984).
15. B. Das and B. Venkataiah, *Biochem. Sys. Ecol.*, **29**, 213 (2001).
16. Z. Lin-gen, O. Seligmann and H. Wagner, *Phytochemistry*, **22**, 617 (1983).
17. F. Cottiglia, L. Bonsignore, G. Loy, D. Garau, C. Floris and M. Casu, *Magn. Reson. Chem.*, **40**, 551 (2002).
18. B. Proska, D. Uhrin, S. Narantuyaa and D. Batsuren, *Pharmazie*, **45**, 804 (1990); S. Mandal, P.C. Das, P.C. Joshi and A. Chatterjee, *Indian J. Chem.,* **30B**, 712 (1991); P.C. Das, P.C. Joshi, S. Mandal and A. Chatterjee, *Indian J. Chem.,* **31B**, 342 (1992); A. Chatterjee, P.C. Das, P.C. Joshi and S. Mandal, *J. Indian Chem. Soc.*, **71**, 475 (1994).
19. L.J. Lin and G.A. Cordell, *J. Chem. Soc., Chem. Commun.*, 160 (1984).
20. A.B. Ray, S.K. Chattopadhyay and S. Kumar, *Tetrahedron*, **41**, 209 (1985).
21. T. Shamsuddin, W. Rahman, S.A. Khan, K.M. Shamsuddin and J.P. Kintzinger, *Phytochemistry*, **27**, 1908 (1988).
22. B.I. Fozdar, T. Shamsuddin, S.A. Khan, K.M. Shamsuddin and J.P. Kintzinger, *Phytochemistry*, **28**, 2459 (1989).
23. N. Ullah, S. Ahmad, P. Muhammad, Z. Ahmad, H.R. Nawaz and A. Malik, *Phytochemistry*, **51**, 103 (1999).
24. B. Das, A. Kashinatham and B. Venkataiah, *Nat. Prod. Lett.*, **13**, 293 (1999).
25. X.F. Cheng and Z.L. Chen, *Fitoterapia*, **71**, 341 (2000).
26. K. Iqbal, I. Anis, N. Mukhtar, A. Malik, N. Fatima and M.I. Chaudhary, *Heterocycles*, **60**, 151 (2003).
27. V.U. Ahmad, F. Ullah, J. Hussain, U. Farooq, M. Zunair, M.T.H. Khan and M.I. Choudhary, *Chem. Pharm. Bull.*, **52**, 1458 (2004).
28. Y.C. Chen, M.J. Cheng, S.J. Lee, A.K. Dixit, T. Ishikawa, I.L. Tsai and I.S. Chen, *Helv. Chim. Acta*, **87**, 2805 (2004).
29. A. Magalhaes, M.D.G.B. Zoghbi and A.C. Siani, *Nat. Prod. Res.*, **20**, 43 (2006).
30. J.F. Xu, Z.M. Feng, J. Liu and P.C. Zhang, *Chem. Biodiv.*, **5**, 591 (2008).
31. S. Michalet, L.P. Fattaccioli, C. Beney, P. Cegiela, C. Bayet, G. Cartier, D. Noungoue-Tchamo, E. Tsamo, A. Mariotte and M.G. Dijoux-Franca, *Helv. Chim. Acta*, **91**, 1106 (2008).
32. Z. Ma, X. Zhang, L. Cheng and P. Zhang, *Fitoterapia*, **80**, 320 (2009).
33. N. Ahmad, F. Zeb, I. Ahmad and F. Wang, *Bioorg. Med. Chem. Lett.*, **19**, 3521 (2009).
34. A. Arnoldi, A. Arnone and L. Merlini, *Heterocycles*, **22**, 1537 (1984).
35. H. Tanaka, I. Kato and K. Ito, *Chem. Pharm. Bull.*, **33**, 3218 (1985).
36. L.-J. Lin and G.A. Cordell, *J. Chem. Soc., Chem. Commun.*, 377 (1986).
37. H. Tanaka, I. Kato and K. Ito, *Chem. Pharm. Bull.*, **34**, 628 (1986).
38. H. Tanaka, M. Ishihara, K. Ichino and K. Ito, *Heterocycles*, **26**, 3115 (1987).
39. H. Tanaka, M. Ishihara,, K. Ichino and K. Ito, *Chem. Pharm. Bull.*, **36**, 1738 (1988).
40. H. Tanaka, M. Ishihara, K. Ichino and K. Ito, *Chem. Pharm. Bull.*, **36**, 3833 (1988).
41. H. Tanaka, M. Ishihara, K. Ichino and K. Ito, *Heterocycles*, **27**, 2651 (1988).
42. X. Ren, X. Chen, K. Peng, X. Xie, Y. Xia and X. Pan, *Tetrahedron*: *Asymm.*, **13**, 1799 (2002).
43. S.P.S. Khanuja, A. Pal, S.K. Chattopadhyay, M.P. Darokar, R.P. Patel, A.K. Gupta, A.S. Negi, T. Kaur, S. Tandon, A.P. Kahol and A. Garg, US Patent 0258989 (2007).
44. V. A Kurkin, *Chem. Nat. Compd.*, **39**, 123 (2003).