

Recent Method For Synthesis Of Coumarin derivatives using Grignard Reagent and Their New Application

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Abstract:

A number of 8-substituted Coumarins (14-19) 2,2 – benzopyran derivatives (5-9), α,β unsaturated ketones (10-13) with E configuration were synthesized using Grignard reagents. Natural product Murralongin (20) has been synthesized by Selenium Dioxide oxidation of compound (19).

Keywords: benzopyran, Coumarin, chemoselectivity, derivatives, Grignard, unusual

Introduction:

Coumarins, a naturally occurring compounds distributed in plant families^{1,2} Coumarins bearing various types of side chains at position 8 and position 4 constitute a well defined family having a vast member of such phytochemicals and enlisted with other diversified natural products^{3,4}. It has been seen from the literature that various types of side chains can be developed at position 8 of Coumarin using Claisen rearrangement and Reformatsky Reaction. This prompted us to undertake a systematic investigation of Grignard reaction^{5,6} on Coumarinyl 8- aryl /acyl ketones and 8-formyl Coumarin. Grignard Reagents find almost routine use due to their high degree of chemo-selectivity^{7,8} The reaction of Grignard Reagents with 7-methoxy-8-acetyl Coumarin showed unexpected chemoselectivity and unusual products formation due to participation of oxygen⁹ and require further studies. Recently studies of various Grignard Reagents on 7-methoxy-8-coumarinylaryl ketones (1 & 2) with Grignards show encouraging results and the products isolated are 2-2-disubstituted chromenes (5-9), unsaturated ketones (10-13) and alcohols (14-19). This encouraging results prompted us to carry further studies on Coumarins (3, 4) using RMgX (R = Et, iso Pr) afforded the alcohols (16-19) as major products together with unsaturated Ketones (10-13) The products isolated (19) can be used for the synthesis of natural product Murralongin (20) isolated from *Murraya Exotica* The compound (19) on Selenium dioxide oxidation¹⁰ afforded the product (20) which is similar to Murralongin and is confirmed by physical and spectral data.

Results and Discussion:

The products isolated from Grignard reaction were subjected to UV and IR spectral studies. The compounds (5-9) exhibit UV absorption at 307 (log ϵ 3.48 to 305 (log ϵ 3.70) and 2.62 (log ϵ 3.89) to 2.95(log ϵ . 3.67) suggest that the compounds (5-9) contain benzopyran and carbonyl chromophores. IR spectral data of the compounds (14, 17, 18) show IR absorption band 3545-3560 cm⁻¹ indicate the presence of alcoholic hydroxy group. and 1710 – 1722 cm⁻¹ indicate the presence of unsaturated. Lactone moiety (14-20). and 1674-1680 cm⁻¹ for unsaturated ketones . and 3675-3680 cm⁻¹ for phenolic OH group (10-13). In NMR spectral data showed that the. Benzylic -OH proton of the compounds (14-18) have been recorded as broad singlet/doublet in the downfield region & 5.75-5.84 demanding intramolecular H-bonding with oxygen at 1' position. The respective methyne proton of CHMe2 appears as doublet-heptet with doublet J = 2Hz demanding long range coupling with -OH proton. On the other hand, in (16) it is further interesting to note that the coupling is enjoyed by one of the diastereotopic proton appear as doublet quartet with one of the doublet coupling is 2Hz whereas the other proton appear as doublet quartet J = 8Hz. The conjugation of double bond between C1-C2 of unsaturated ketones, (10-13) assigned as E-configuration ¹¹ ¹². Finally NOE studies confirm the E-configuration of the double bond of unsaturated ketones.as the coupling constant is 16.9Hz. Finally the enhancement in the intensity of 1'-H observed in compound (11) on irradiation of 3'-methylene proton during NOE studies which confirm the close proximity of 1'-H and COCH₂CH₂Me group. Similarly NOE studies of compound (20) suggest that 1'C

Experimental Procedure :

All M.P and B.P are uncorrected. IR spectra were recorded on Hitachi 270-30 Spectro photo meter, ¹H NMR , ¹³C NMR spectra were recorded on a Bruker WH 250 spectro photo meter and mass spectra on Finnigan Mat 1020 operating on 70 eV.

Grignard reaction on Coumarins (1) or (2) or (3) or (4):

Various Grignard Reagents (RMgX , R= Et, ¹Pr , ⁿBu , Ph) were prepared in the usual way under nitrogen atmosphere. The respective Grignard (6 m.moles) thus prepared was added to respective Coumarins (4 m.moles) of (1) or (2) or (3) or (4) in THF solution slowly with stirring under nitrogen atmosphere for 0.5 hours and kept at room temperature with stirring for 6 hours. The respective reaction mixture were acidified with cold dilute 20% HCl and extracted with Chloroform. The Chloroform layer then washed with brine solution and dried over anhydrous sodium sulphate. Evaporation of solvent afforded the crude products. The crude products obtained from (1),(2),(3),(4) in each experiment on chromatographic separation furnished (5 – 13) from (1) & (2) and (14-19) from (3) and (4).

Preparation of Murralongin (20) from compound (19)

A Mixture of compound [(19) : 4 M.mole] and selenium dioxide (6 M.mole) in 50ml Glacial acetic acid were refluxed for 5 hours. Thus the hot reaction mixture was filtered through silica gel. The filtrate was concentrated to 2 ml and extracted with chloroform. The chloroform layer was evaporated to give crystalline solid (20) , m.p 100^o C.

Spectroscopic data of New Compounds:

[5] m.p- 210, C, yield-11%. IR:1672,1628,1601cm⁻¹.PMR3.66 (3H,s,7-OMe), 6.00 (1H, d, J = 9Hz, 3-H), 6.46(1H, d, J = Hz, 5-H), 6.64 (1H, d, J = 9Hz, 4-H), 7.06 (1H, d, J = 8Hz, 5-H), 7.12 (10H, s, Ph₂ at C₂), 7.32 (2H, btJ = 7-Hz, 3'-H, 5'-H),7.50 (1H, bt, J = 7Hz, 4'-H), 7.74 (2H, dd, J = 7 & 2Hz, 2'-H, & 6'-H). MS: 418 (47, M+), 493 (13 -Me), 387 (10M+ -M+ -OMe), 341 (100, M + -Ph) 313 (2M+ -COPh), 297(16), 239(5) 195(Ph CO+), 77 (4, Ph+)

[6] M.P- 136°C Yield: 49% IR: 1676, 1604 cm⁻¹(6): 2.12 (3H, d, J=1 Hz, 4-Me), 3.65 (3H, s7 OMe), 3.80 (1H, q, J=1Hz, 3H) 6.48(1H, d, J = 8Hz, 6H),7.10 (10H, bs, Ph₂), 7.20, J = 8Hz, 5-H), 7.30 (2H, bt, J = 7Hz, 3'-H, 5-H), 7.50 (1H, bt, J = 8-Hz, 4 H7.72 (2H, dd, J = 8 & 2 Hz 2'-H, 6-H). ¹³C N MR: 82.5 (q, C-2), 103.2 (t, C-3) 128.4 (q, C-4), 117.2 (q, C-4a), 125.8 (t, C-5), 124.3 (t, C-6), 157.7(q, C7), 122.2 (q, C-8) 152.2 (q, C-8a), 138.1 (q, C-1') 129 (t, C-2') 128.2 (t, C-3'), 133.1 (t,C-4'), 55.8 (p, O Me) 18.1 (p, 4-Me), 195 (q, 8-CO)

[7] M.P: 166° C Yield: (50%) IR: 1676, 1604cm⁻¹. PMR 0.69 (6-H, t, J = 7.4Hz, 2Me of 2Etat C-2) ,1.44 (4H, comp, two methylene of two Et at C-2), 2.02 (3H, d, J = 1Hz, 4 - Me) 3. 71(3H, s, 7- OMe), 5.15 (1H, br. q, J = 1.4 Hz, 3 - H), 6.45 (1H, d, J = 8.5 Hz, 6 - H), 7.13 (1H, J = 8.5 Hz, 5-H), 7.42 (2H, t, J = 7Hz, 3' H,7.54 (1H, tt, J = 7.0 & 2.0, 4-H), 7.88 (2H, dd, J = 7.0 & 2.0 Hz, 2'-H, 6'-H)¹³ C NMR: 82.3 (q, C-2), 102.3 (t, C-3), 128 (q, C-4), 116.1 (q, C-4a), 124.4 (t, C-5), 123.2 (t, C-6), 157.5 (q, C-5), 122.3 (q, C-8), 152.2 (q, C-8a), 138.1 (q, C-1'), 129.4 (t, C-2'), 128.3 (t, C-3'), 133.0 (t, C-4'), 55.7 (p, 7-OMe), \ 18.1 (p, 4-Me). 195.6 (q, 8-CO), 32.0 (s \ 2 - CH₂ CH₃), 7.52 (p, 2-CH₂ CH₃) MS: 336(20, M+), 318 (73, M+ -Me), 278 (30, M+ -2 -C₂H₅), 259 (100, M+ -Ph), 231 (80, M+ -Ph CO), 218 (31)

[8] M.P+167°C Yield 28% IR:1668, 1600 cm⁻¹P MR: (8): 0.72(6H, t, J = 7.3Hz, two Me of two n -pr at C -2), 1.17(4H, comp. multiplet, two CH₂CH₂ Me), 1.38(4H, m, two CH₂CH₂ Me) 2.10 (3H, d, J = 1.4Hz, 4-Me) 3.70 (3H, s, 7OMe), 5.14 (1H, q, J = 1.4Hz, 3-H), 6.45 (1H, d, J = 8Hz, 6 -H), 7.11 (1H, J = 8.5Hz, 5-H) 7.41 (2H, bt, J = 7Hz, 1'-H, 5'-H) 7.52 (1H, tt, J = 7.0 1.5 Hz, 4' -H), 7.86 (2H, dd, J = 7.0 & 1.5 Hz, 2'-H, & 6'-H).

[9] M.P: 117°C, Yield: 29% IR: 1675, 1596 cm⁻¹. PMR: 0.74 (6-H, t , J = 7Hz, two Me gr of n Bu at C-2), 1.14 (8H, compl, two methylene proton of n-Bu), 1, 28 -1.68 (4-H, br.compl two methylene proton, n Bu). 2.04 (3-H, d J = 0.5 Hz, 4-Me), 3.72 (3H, s, 7-OMe) 5.16 (1H, bs, 3-H), 6.44 (1-H, d, J = 8Hz, 6-H) 7.12 (1-H, d, J = 8Hz, 5-H), 7.48 (3H, compl, 3'-H, 4'-H, 5'-H), 7.90 (2H, dd, J = 7 & 2Hz 2'-H, & 6'-H).

[10] M.P; 137°C Yield: 44%, IR: 3456, 1678, 1658, 1602 PMR: 3.55 (3H, s, 7-OMe), 7.42 -7.60 (6H, compl, Ar- protons of two phenyl gr,), 7.70 (1H, d, J = 16Hz, 2'-H), 7.72 (1 H, d, J = 8Hz, 5-H), 8.02 (1H, d , J = 16Hz, 1'-H) 7.90-7.98 (4H, dd J = 10, 2Hz, ortho Ar -proton of two phenyl group) 11.78 (1H, s, Phenolic - OH MS: 308 (11, M+), 293 (100, M+ -Me), 277 (1, M+ OMe), 263 (1, M+ -Me & HCHO), 249

[11] MP: 96°C, Yield: 25% IR: 3450, 1694, 1610 cm⁻¹.1.12 (3H, t, J = 7Hz, COCH₂ Me), 2.66 (2H, q, J = 7Hz, COCH₂ Me), 3.52 (3H, s 7- OMe), 6.44 (1H, d, J = 7Hz, 4 -H), 6.75(1H, d,J = 17Hz, 2''-H), 7.36-7.60 (3Hcompl, 3'-H, 4'-H, & 5'-H) 7.64 (1H, d, J = 8Hz, 5-H), 7.69 (2H, dd, J = 7 &1.5Hz, 2'-H & 6'-H), 7.84 (1H, d, J = 16Hz, 1''-H) 11.48 (1H, s, Phenolic OH)

[12] M.P: 112°C Yield: 32% I.R: 3564, 1690, 1603 cm⁻¹ PMR: 0.94 (3H, t, J = 7Hz, COCH₂CH₂ Me), 1.68 (2H, sextet, J = 7Hz COCH₂CH₂ Me), 2.6 = (2H, t, J = 7Hz, COCH₂CH₂ Me), 3.52 (3H, s, OMe), 6.44 (1H, s,

d, J = 8Hz, 4-H), 6.76 (1H, d, J = 16Hz, 2''-H), 7.36 -7.56 (4H, compl 3'-H, 4'-H, 5'-H, & 5-H), 7.68 (2H, d, J = 8Hz, 2'-H, 6-H), 7.86 (1H, 1H, J = 16Hz, 1'-H) TV11.52 (1H, s, Phenolic OH).

[13] IR: 3455, 1720, 1600 .cm⁻¹ M.P -98°C, Yield: 38% I.R: 3455, 1720, 1600 cm⁻¹ PMR: 0.83 (3H, dist, t, J = 7Hz, CO CH₂ CH₂CH₂ Me) 1.32 (2H, sextet, J = 7Hz, COCH₂ CH₂ CH₂ Me), 1.62 (1H, quin, J = 7Hz, CH₂ CH₂ CH₂ Me), 2.64 (2H, t, J = 7Hz, CH₂ CH₂ CH₂ Me), 3.52 (1H, s, OMe), 6.44 (1H, d, J = 7Hz, 4-H), 6.76 (1H, d, J = 16Hz, 2''-H), 7.36 -7.56 (4H, compl, 3- H, 4 -H, 5 H), 7.68 (2H, d, J = 7-Hz, 2' +H, 6 -H), 7.84 (1H, d, J = 17Hz, 1'-H), 11.43 (1H, s, Phenolic OH)¹³C NMR: 160.1(q, C-2), 103.2 (t, C-3) 128.4 (q, C-4), 117.2 (q, C -4a), 124.3 (t, C-5) 124.0 (t, C-6) 157.7 (q, C-7), 117.7 (q, C-8), 150.6 (qC-4a), 137.0 (q, C1'), 19.5(q, C-2') 128.3 (t, C-3') 132.2 (t, C-4'), 55.6 (p, 7 -OMe) 195.2 (q, 8 -CO), 42.2 (s, CH₂ CH₂ CH₂ Me) 16.2 (s, 2-CH₂ CH₂ CH₂ Me) 14.1 (p, 2-n n-Bu Me).

[14] M.P -142°C, Yield -31%. IR: 3551, 1728, 1598 cm⁻¹ PMR 0.85 (3H, t, J = 7Hz, Me grof 8CH (OH), 2.04 (1H dq, J = 7Hz, Ha of 2'-H) 2.63 (2H, ddq, J = 7 & 1.5 Hz, 2'-Hb) 3.63 (3H, s, OMe), 5.38 (1H, d, J = 4Hz 1'-H), 5.71 (1H, br.d, 3-H), 5.86 (1H, brs, 3-H), 6.52 (1H, d, J = 8.5Hz, 6-H), 7.00 (1H, d, J = 8.5Hz, 5-H), 7.10 (1H, d, J = 8.5Hz,4-H)

Table: Compound (14)

Cross peaks (Δ ¹H vs ¹³C) in HMQC spectroscopy

Proton attached (Chemical shift)	Carbon attached (Chemical shift)
2' -Me of C-8 (0.85)	C-1'of C-8 (9.28)
Ha of 2'of C-8 (2.04)	C-2' of C-8 (36.06)
Hb of 2' at C-8 (2.62)	C-2'of C-8 (36.06)
7-OMe (3.63)	7 -OMe (55.92)
1'-H of. C -1' (5.35)	C-1' at C-8 (80.4)
3-H (5.86)	C-3 (123.0)
6-H (6.52)	C-6 (105.18)
5-H (7.00)	C-5 (124.4)

MS spectra by electron spray ionization of the compound (14) m/z ion peak [M +Na] + at m/z-234.06

[15] M.P -112°C Yield: 25% IR: 3552, 1720, 1610, 1598 cm⁻¹. PMR: 0.79 (3H, d, J = 8Hz, Me gr of C-8 side chain), 1.10 (3H, d, J = 7Hz, Me gr of iso -pr), 3.58 (1H, heptet, J = 6, & 2Hz. CH Me₂), 3.83 (3H, s OMe), 5.44 (1H, d J = 4Hz, 1'-H) 5.85 (1H, d, J = 7Hz alcoholic OH 7.36 -7.12 (2H, compl. 3-H, 4-H), 6.87 (1H , d, = 9Hz 6-H), ¹³C NMR: 160.5 (q, C-2), 109.3 (t, C-3), 151.6 (q, C-4) 115 (q, C-4a), 124.5 (t, C-5), 112.3 (t, C-6) 160.9 (q, C-7), 123.9 (C-8), 152.8 (qC-8a) 147.5 (q, C1'), 125.4 (t, C-2') 126.3 (t, C-3') 127.5 (t, C-4'), 56.6 (p, 7 -OMe), 82.2 (q, .8 -C -OH). 36.2 (t, CH Me₂), 19.9 & 16.8 (p, CH Me₂).

[16] M.P: 85°C Yield: 17% (16) IR, 1720, 1600 cm⁻¹ MR: 1.6 (3H, d, l = 8Hz, 8 -C (Me) = CH Me), 2.38 (3H, d, J = 17Hz, 1'-Me), 3.48 (3H, s, OMe), .623 (1H, d, J = 7Hz, 2'-H), 5.51 (1H, q, J = 7Hz, C(Me) =CH

Me), 6.94 (1H, d J = 7Hz, 4-H), 5.90 (1H, s, 1'-H), 6.90-7.28 3H, compl m, 3-H, 6-H, 5-H) MS: 295 (100, M+ -CH (Me)₂, 217 (85, m/z 296 -C₆H₅), 199, 17, m/z, 217 +CO), 131 (5) m/z, 146 -Me), 105 (14, Ph CO+)

[17] M.P: 102°C, Yield: 42%. IR: 3550, 1718, 1601 cm⁻¹ PMR: 0.92 (3H, t, J = 7Hz, 2' Me), 2.36 (3H, d, J = 9.6Hz, 1' -Me) 2.12 & 2.56 (each 1H dd, J = 2, 9Hz, 2'Ha, 2'Hb), 3.76 (3H, s, OMe), 5.10 (1H, s, OH), 7.18 & 6.72 (1H, d, J = 10Hz, H-5, H-6), 7.29 & 7.41 (each 1H, d, J = 12Hz, H-4, H-3)

[18] M.P -97°C, Yield- 23%. In IR: 3550, 1728, 1602, cm⁻¹ PMR: 1.28 (3H, t, J = 8Hz, 1'-Me), 1.82 (6H, d, J = 7Hz, two 2' -Me), 3.50 (1H, d hept, J = 6, 2Hz 2'H of CHMe₂), 3.70 (3H, s, 7-OMe) 5.10 (1H, s, OH), 5.40 (1H, d, J = 4Hz, 2'-H) 7.15 & 6.72 (each 1H, d, J = 10Jz, H-5, H-6), 7.68 & 7.18 (each 1H, d, J = 7Hz, H-4, H-3)¹³C.N MR: 159.2 (C-2), 108.6 (C-3), 149.3 (C-4) 116.4 (C-4a), 125.0 (C-5), 105.0 (C-6), 157.8 (C-7), 116.0 (C-8), 135.4 (C-8a) 56.8 (7-OMe) 135.8 (C-1') 105.8 (C-2'), 32.3 (1'-Me), 14.3 (2'Me), 13.6 (2'-Me). MS: 262(M+), 247(M+ -Me,), 244 (M+ -H 2O) 226 (M+ -CO, H₂O), 231(M+-OMe)

[19] M.P- 88°C, Yield: 28% IR: 1713, 1618, 1600 cm P MR: 1.70 (3H, s, 2' Me), 1.8 (3H, s, Me), 2.39 (3H, s, 1'Me), 3.92 (3H, s, OMe), 6.90 & 7.24 (each 1H, d, J = 9.8 Hz ,H-5 H-4) 7.74 & 7.16 (each 1H, d, J = 9.6 Hz, H-3, H-6). MS: 244 (100, M+), 229 (85, M+ -Me), 215 (70, M+ -CO, -Me 199 (25)¹³C NMR: 159.9 (q, C-2), 115.2 (t, C-3), 151.0 (q, C-4), 115.1 (q, C-4a), 124.8 (t, C-5), 112.0 (t, C-6) 159.7 (q, C-7) 119.2 (q, C-8), 152.1 (q, C-8a) 56.8 (p, .7- OMe), 107 (q, 8 -C = C), .32.1 (t, 1'Me 14.2 (t, 2' Me₂). MS: 244 (M+100), 229 (M+ -Me), 214 (M+ -2Me) 216 (M+ -CO), 201 (M+ -CO, Me)

[20] M.P-135°C, Yield: 60% IR: 1722, 1670, 1602 PMR: 1.76 (3H, d, J = 0.5Hz, 1' -Me), 2.40 (3H, s, 2'Me), 3.90 (3H, s, OMe), 6.90 & 7.27 (each 1H, d, J = 9.8Hz, H-5, H-4) 7.2 & 7.74 (each 1H, d, J = 9.6Hz, H-3, H-6) 10.2 (1H, s, CHO). MS: 258 (M+ 100%), 243 (M+ -Me), 229(M+ -CHO), 227 (M+ -OMe)¹³C NMR: 199.8 (2°, CHO), 159.2 (4°, C-7) 152.2 (3°C4a), 149.1(3°C-8a), 142.1 (3°C -1'), 127.8 (3°C-2'), 127.0 (3°C-5), 123.1 (3°,C-3), 122.9 (4°,C-8), 121.2 (4°C,-4), 117.4 (4°, C-4a), 105.6 (3°,C-6) 80.4 (4°C-1'), 55.95 (1°, 7-OMe), 29.9 (1°, 1'-Me), 23.8 (1°, 2' -Me).

HMQC spectral studies of Compound (20)

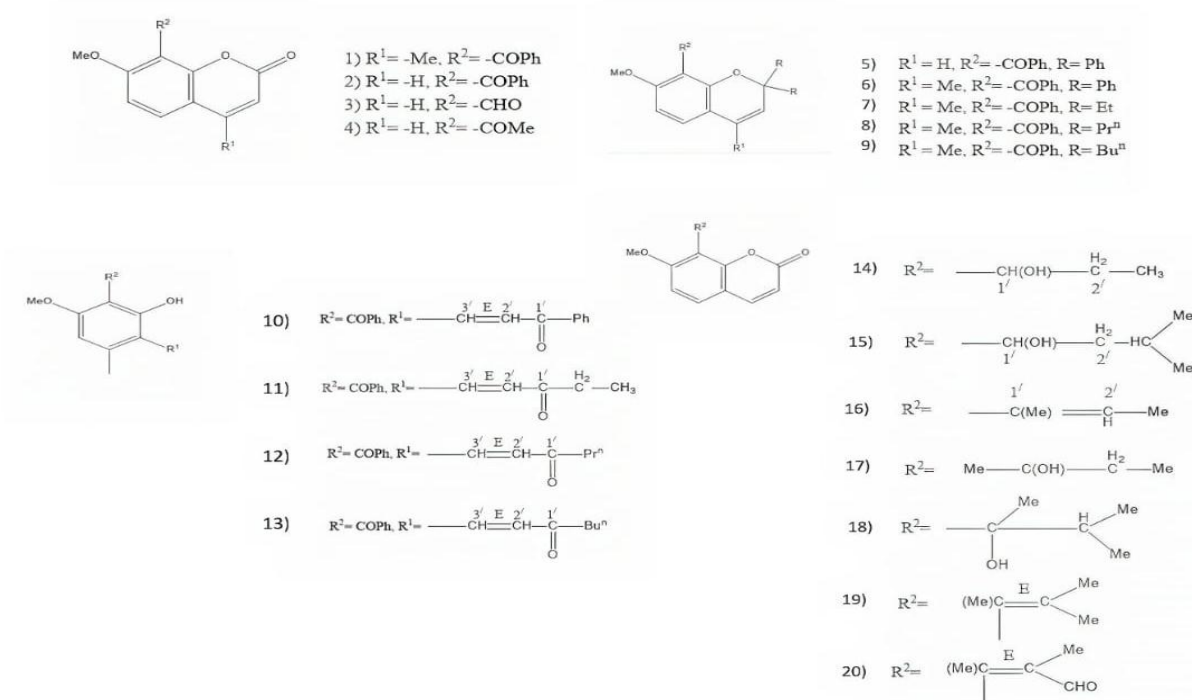
Cross peaks of chemical shift ¹H vs ¹³C

Proton attached on ()	Carbon attached on ()
8-1' Me(1.76)	1' at C- (29.8)
8-2' Me (2.40)	2' - C (23.8)
7 - Ome (3.90)	7 OMe (55.9)
4-H (6.90)	C-4 (122.9)
5-H (7.00)	C-5 (127.6)
3-H (7.28)	C-3 (123.6)
CHO (10.2)	C-3' (199.8)

Elemental analysis of compounds (5-20):

Compound	Molecular Formula	Elemental Analysis (%)		Found	
		C	H	C	H
(5)	C ₂₉ H ₂₂ O ₃	83.25	5.1	83.1	5.04
(6)	C ₃₀ H ₂₄ O ₃	83.32	5.55	83.36	5.22
(7)	C ₂₂ H ₂₄ O ₃	78.57	7.14	78.02	7.20
(8)	C ₂₄ H ₂₈ O ₃	79.12	7.69	78.98	7.60
(9)	C ₂₆ H ₃₂ O ₃	79.59	8.16	79.70	8.11
(10)	C ₂₃ H ₁₈ O ₄	77.09	5.02	78.00	5.22
(11)	C ₁₉ H ₁₈ O ₄	73.54	5.80	73.20	6.71
(12)	C ₂₀ H ₂₀ O ₄	74.07	6.17	73.88	6.50
(13)	C ₂₁ H ₂₂ O ₄	74.55	6.50	74.20	6.51
(14)	C ₁₃ H ₁₄ O ₄	66.66	5.98	66.00	6.11
(15)	C ₁₄ H ₁₆ O ₄	67.74	5.74	66.88	5.80
(16)	C ₁₄ H ₁₄ O ₃	73.04	6.95	74.01	7.12
(17)	C ₁₄ H ₁₆ O ₄	67.75	5.64	67.90	5.70
(18)	C ₁₅ H ₁₈ O ₄	68.70	6.87	68.82	6.42
(19)	C ₁₅ H ₁₆ O ₄	73.77	6.55	73.52	6.31
(20)	C ₁₅ H ₁₄ O ₄	69.74	5.42	68.61	5.44

Structure of the Compounds:-



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All new compounds gave expected- UV, IR, NMR, Elemental Analysis.