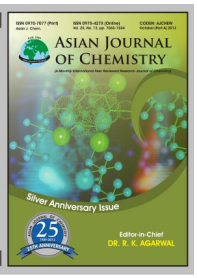
Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8780-8784

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15615



Chemical Constituents and New Xanthone Derivatives from *Mesua ferrea* and *Mesua congestiflora*

S.S. TEH[1], G.C.L. EE[1,*] and S.H. MAH[1,2]

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[2]School of Biosciences, Taylor's University, Taylor's University Lakeside Campus, 47500 Subang Jaya, Malaysia

*Corresponding author: Fax: +60 3 89465380; Tel: +60 3 89466785; E-mail: gwen@science.upm.edu.my

(*Received*: 10 April 2013; *Accepted*: 29 August 2013) AJC-14048

The phytochemical study on the root bark of *Mesua ferrea* and the roots of *Mesua congestiflora* resulted in the isolation and identification of nine compounds. Seven xanthones isolated from the root bark of *Mesua ferrea* were mesuaferrin A (**1**), mesuaferrin B (**2**), mesuaferrin C (**3**), caloxanthone C (**4**), macluraxanthone (**5**), 1,5-dihydroxyxanthone (**6**) and tovopyrifolin C (**7**). Meanwhile, *Mesua congestiflora* afforded one benzophenone, congestiflorone (**8**) together with a xanthone α-mangostin (**9**). The structural modification reactions were also carried out to obtain two new compounds which are caloxanthone C diacetate (**10**) and congestiflorone acetate (**11**). The characterizations of these compounds were achieved through a variety of spectroscopic techniques such as 1D and 2D NMR, UV, IR and GC-MS.

Key Words: Xanthone, Benzophenone, Acetate, *Mesua ferrea*, *Mesua congestiflora*.

INTRODUCTION

Mesua, a genus of flowering plants in the Clusiaceae family, is native to tropical southern Asia. *Mesua ferrea* is native to tropical Sri Lanka but it is also widely cultivated in India and south tropical Asia. Common names for this species are Ceylon ironwood, Indian rose chestnut and Cobra's saffron. The local Malaysian names for this species are penaga and nahar. Different parts of *Mesua ferrea* are traditionally used in folk medicine for the treatment of dyspepsia, fever and renal diseases and it can even act as a poultice[1]. The flowers are traditionally used in conditions like asthma, cough and fever whereas the fresh flowers are useful in reducing itchiness and nausea. Previous studies on *Mesua ferrea* blossoms have indicated it to have a potential in pharmaceutical development. *Mesua congestiflora* is native to Indonesia and Borneo. It is a medium sized tree that can only develop to 15 m in height The tree contains yellow resins and the fruit is brown in colour. Although a number of *Mesua* species have been formerly investigated only a few were studied in detail. Phytochemical investigations on different parts of the *Mesua* plants show the occurrence of xanthones[2-6], coumarins[2,7-10], biflavones, cyclohexanedione derivatives and essential oils[1,8]. This research attempts to extract phytochemicals from *Mesua ferrea* and *Mesua congestiflora* and derivatize them to obtain acetate compounds for further pharmacological studies. Seven xanthones (**1**-**7**) were isolated from the root bark of *Mesua ferrea*. The investigation of *Mesua congestiflora,* on the other hand led to the isolation of a benzophenone, congestiflorone (**8**) and a xanthone α-mangostin (**9**). The acetylation reaction of caloxanthone C (**4**) and congestiflorone (**8**) gave two new compounds which were identified as caloxanthone C diacetate (**10**) and congestiflorone acetate (**11**).

EXPERIMENTAL

The root bark of *Mesua ferrea* was collected from campus grounds in Universiti Putra Malaysia, Serdang, Selangor, Malaysia while the roots of *Mesua congestiflora* were collected from the Kuching district in Sarawak, Malaysia. All the plant materials were identified by Associate Professor Dr. Rusea Go, Department of Biology, Faculty of Science, Universiti Putra Malaysia and deposited in the herbarium of the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia.

Infrared spectra were measured using the universal attenuated total reflection (UATR) technique on a Perkin-Elmer 100 Series FT-IR spectrometer. EIMS were recorded on a Shimadzu GCMS-QP5050A spectrometer. NMR spectra were obtained using a Unity JEOL 500 MHz FTNMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Ultraviolet spectra were recorded in EtOH on a Shimadzu UV-160A, UV-visible recording spectrophotometer.

Extraction and isolation: The 3 kg milled, air-dried and powdered *Mesua ferrea* root bark was defatted with *n*-hexane and extracted sequentially with dichloromethane, ethyl acetate and methanol. The extract solutions were concentrated and

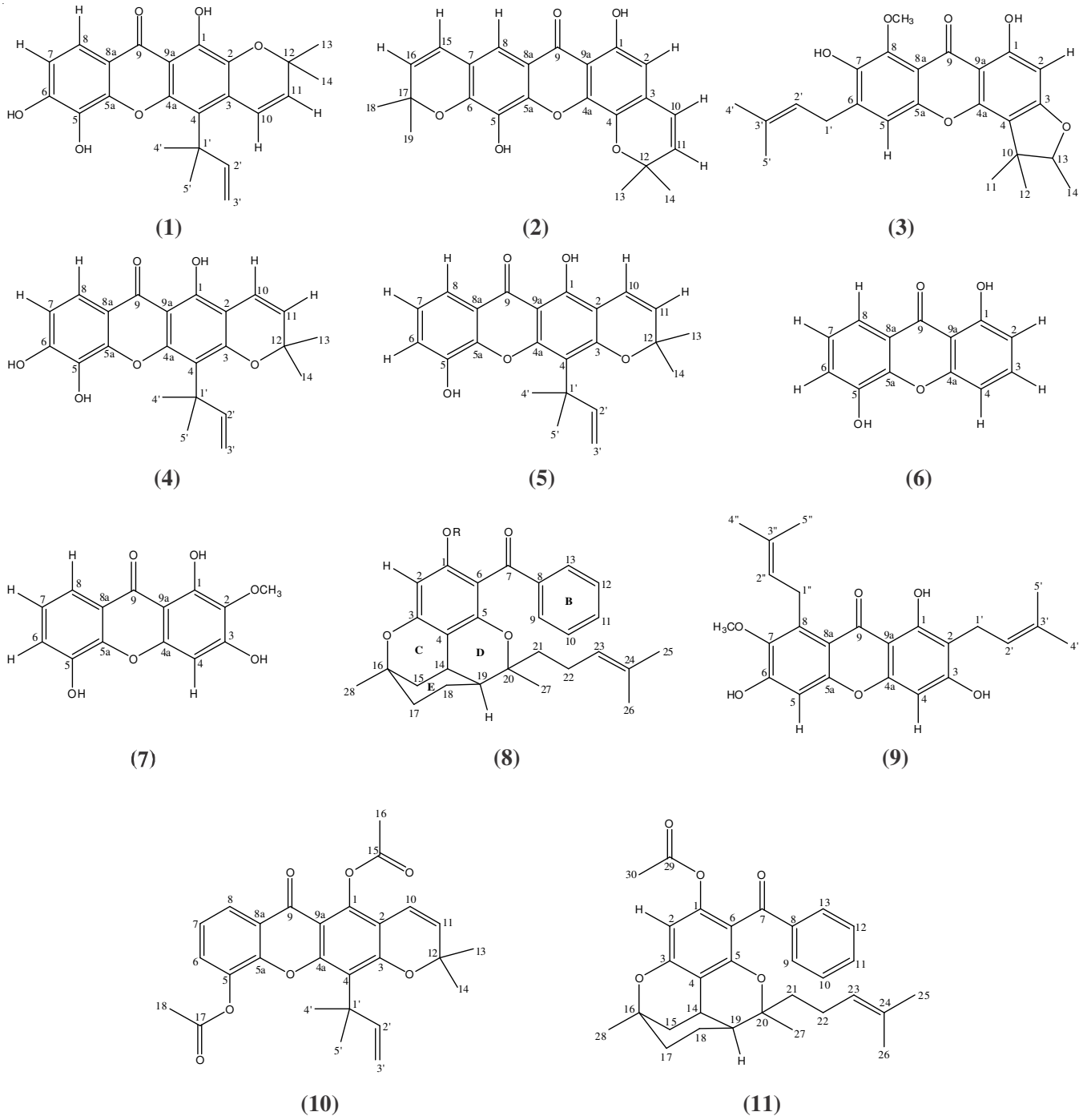


Fig. 1. Structures of compounds **1-11**

dried using a rotary evaporator to give hexane (49.6 g), dichloromethane (19.5 g), ethyl acetate (16.7 g) and methanol (62.2 g) extracts. Column chromatographic separation of the hexane extract yielded six compounds which were identified as mesuaferrin A (**1**) (20 mg), mesuaferrin C (**3**) (10 mg), caloxanthone C (**4**) (48 mg) and macluraxanthone (**5**) (50 mg). Meanwhile, the dichloromethane extract gave mesuaferrin B (**2**) (22 mg) only while the ethyl acetate extract furnished two xanthones which were 1,5-dihydroxyxanthone (**6**) (3 mg) and tovopyrifolin C (**7**) (3 mg). The 0.84 kg milled roots of *Mesua congestiflora* were macerated consecutively with *n*-hexane, ethyl acetate and methanol at room temperature. The extracts were dried under reduced pressure using a rotary evaporator to yield hexane (5.5 g), ethyl acetate (61.0 g) and methanol (120.5 g) extracts. Column chromatographic separation of the hexane extract afforded a benzophenone, congestiflorone (**8**) (65 mg) and a xanthone α-mangostin (**9**) (15 mg).

Structural modifications of compounds 4 and 8: Compounds **4** and **8** were acetylated. A solution of 40-50 mg of pure compound in 15 mL of pyridine was added to 15 mL of acetic anhydride (Ac_2O) and heated in a water bath at 80 ºC for 6 h. The reacted mixture was then dried under reduced pressure using a rotary evaporator. The product was chromatographed over a silica gel column using a stepwise

gradient system to obtain the pure acetate compound. Compound **10** was obtained from the acetylation reaction of pure caloxanthone C (**4**) (30 mg). The crude product was purified by a series of mini column chromatography by eluting with 50 % hexane/50 % chloroform to yield caloxanthone C diacetate (**10**) (7 mg), a yellowish oil. Compound **11** was obtained from the acetylation reaction of pure congestiflorone (**8**) (55 mg). The crude product was then chromatographed over a silica gel column using a stepwise gradient system to obtain another yellowish oil, congestiflorone acetate (**11**) (6 mg).

Spectral data

Mesuaferrin A (1): Yellow crystals. m.p. 180-181 ºC. UV (EtOH) λ_{max} nm (log ε): 337, 290, 283, 243, 207. IR (KBr, ν_{max}, cm^{-1}): 3334, 2926, 2862, 1728, 1582, 1455 and 1185. MS m/z (rel. int.): 394, 380, 379, 351, 182, 162, 153, 55. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[11].

Mesuaferrin B (2): Yellow crystals. m.p. 245-246 ºC. UV (EtOH) λ_{max} nm (log ε): 345, 298, 290, 208. IR (KBr, ν_{max}, cm^{-1}): 3426, 2925, 2857, 1739, 1640, 1573 and 1158. MS m/z (rel. int.): 394, 380, 379, 351, 182, 162, 153, 55. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[11].

Mesuaferrin C (3): Yellowish oil. UV (EtOH) λ_{max} nm (log ε): 323, 321, 246, 208. IR (KBr, ν_{max}, cm^{-1}): 3345, 2933, 1715, 1633, 1440 and 1172. MS m/z (rel. int.): 410, 395, 379, 368, 367, 337, 176. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[12].

Caloxanthone C (4): Yellow crystals. m.p. 213-215 ºC. UV (EtOH) λ_{max} nm (log ε): 382, 290, 272, 240. IR (KBr, ν_{max}, cm^{-1}): 3431, 2923, 2859, 1722, 1591, 1459 and 1200. MS m/z (rel. int.): 378, 364, 363, 335, 305, 154. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[13].

Macluraxanthone (5): Yellow crystals.m.p. 169-170 ºC. UV (EtOH) λ_{max} nm (log ε): 336, 290, 280, 241. IR (KBr, ν_{max}, cm^{-1}): 3320, 2926, 2860, 1738, 1583, 1454 and 1259. MS m/z (rel. int.): 394, 379, 182, 162. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[14].

1,5-Dihydroxyxanthone (6): Yellow crystals. m.p. 267-269 ºC. UV (EtOH) λ_{max} nm (log ε): 340, 280, 240. IR (KBr, ν_{max}, cm^{-1}): 3450, 2940, 2830, 1710, 1610, 1585 and 1310. MS m/z (rel. int.): 228, 200, 171, 115, 100, 92, 63. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[15].

Tovopyrifolin C (7): Yellow crystals.m.p. 254-256 ºC. UV (EtOH) λ_{max} nm (log ε): 331, 282, 235. IR (KBr, ν_{max}, cm^{-1}): 3440, 2930, 2865, 1703, 1615, 1468 and 1302. MS m/z (rel. int.): 274, 259, 231, 137, 93, 65, 51. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[16].

Congestiflorone (8): Yellow crystals.m.p. 129-130 ºC. UV (EtOH) λ_{max} nm (log ε): 312, 216. IR (KBr, ν_{max}, cm^{-1}): 2925, 1740, 1615, 1458 and 1156. MS m/z (rel. int.): 432, 283, 282, 281, 243, 203, 165, 105, 77, 69, 55. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[17].

α-Mangostin (9): Orange crystals.m.p. 180-182 ºC. UV (EtOH) λ_{max} nm (log ε): 351, 313, 259. IR (KBr, ν_{max}, cm^{-1}): 3401, 2922, 2844, 1720, 1608 and 1459. MS m/z (rel. int.): 410, 367, 355, 339, 311, 285, 162, 55. The ^1H and ^{13}C NMR ($CDCl_3$) spectral data are consistent with published data[18].

Caloxanthone C diacetate (10): Yellowish oil. IR (KBr, ν_{max}, cm^{-1}): 2929 (sp^2 C-H stretch), 2860 (sp^3 C-H stretch), 1772 (C=O stretch), 1597 and 1455 (C=C aromatic), 1189 (C-O stretch). MS m/z (rel. int.): 462 (9), 420 (68), 405 (100), 391 (12), 377 (16), 363 (36), 137 (6). For ^1H and ^{13}C NMR spectra (Table-1).

Congestiflorone acetate (11): Yellowish oil. IR (KBr, ν_{max}, cm^{-1}): 2928 (sp^2 C-H stretch), 1765 (C=O stretch), 1601 and 1435 (C=C aromatic), 1200 (C-O stretch). MS m/z (rel. int.): 474 (17), 432 (12), 325 (31), 281 (100), 281 (100), 243 (13), 203 (23), 165 (10), 105 (44), 77 (16), 69 (25). For ^1H and ^{13}C NMR spectra (Table-2).

RESULTS AND DISCUSSION

Compound **10**, a yellowish oil was synthesized from caloxanthone C (**4**) (30 mg). The EIMS showed a molecular peak at m/z 462 corresponding to the molecular formula $C_{27}H_{26}O_7$. Several significant maximum absorption peaks were observed from the FTIR spectrum which comprises the sp^2 C-H stretching (2929 cm^{-1}), sp^3 C-H stretching (2860 cm^{-1}), C=O group (1772 cm^{-1}), C=C aromatic ring (1597 and 1455 cm^{-1}) and C-O stretching (1189 cm^{-1}). The additional mass of 84 in **10** when compared to caloxanthone C (**4**) in the EIMS as well as the absence of hydroxyl groups in the FTIR spectrum implied that the two OH groups were successfully replaced by two acetyl groups.

The two singlet signals for the hydroxyl groups at δ 13.43 and 6.20 were absent in the ^1H NMR of compound **10**. However, an additional two sharp methyl singlets at high field region which resonated at δ 2.40 and 2.50 were observed.

Furthermore, the ^{13}C NMR spectrum revealed the presence of twenty seven carbon signal in which three were overlapped. The carbon signals were assigned based on the comparison with those of caloxanthone C (**4**). The carbon signals resonated at δ 21.2 x 2, 27.8 x 2 (C-13 and C-14), 29.9 x 2 (C-4' and C-5'), 41.7 (C-1'), 78.4 (C-12), 108.5 (C-3'), 109.4 (C-9a), 112.7 (C-2), 115.7 (C-8), 120.6 (C-4), 123.3 (C-8a), 123.4 (C-10), 123.8 (C-6), 127.8 (C-7), 131.5 (C-11), 138.6 (C-5), 144.2 (C-5a), 147.2 (C-4a), 150.0 (C-2'), 156.2 (C-1), 157.6 (C-3), 169.0, 169.5 and 175.1 (C-9). Four remaining unidentified carbon signals were thus assigned to C-16 (δ 21.2), C-18 (δ 21.2), C-17 (δ 169.0) and C-15 (δ 169.5) as the two downfield signals were due to the presence of carbonyl groups. The combination of ^1H and ^{13}C spectra confirmed that the substitution of the hydroxyl groups at C-1 and C-5 of caloxanthone C (**4**) by two acetyl groups is successful. Thus, this structure was elucidated to be caloxanthone C diacetate (**10**). Table-1 summarizes the 1D NMR data of caloxanthone C diacetate (**10**).

Compound **11** is a yellowish oil obtained from the structural modification of congestiflorone (**8**) (55 mg) which was isolated from *Mesua congestiflora*. Compound **11** has a molecular formula of $C_{30}H_{34}O_5$ with molecular mass of 474 corresponding to a difference of one CH_3CO group from congestiflorone (**8**). The difference could be easily accounted

TABLE-1
^{1}H NMR (500 MHz, $CDCl_3$) AND ^{13}C NMR (125 MHz, $CDCl_3$) DATA OF CALOXANTHONE C DIACETATE (**10**) AND CALOXANTHONE C (**4**)

Position	^{1}H (δ)	*^{1}H (δ)	^{13}C (δ)	*^{13}C (δ)
1	–	–	156.2	156.8
2	–	–	112.7	105.6
3	–	–	157.6	159.5
4	–	–	120.6	113.3
4a	–	–	147.2	154.1
5	–	–	138.6	145.4
5a	–	–	144.2	144.2
6	7.41 (dd, 1H, 8.8, 1.8 Hz)	7.25 (d, 1H, 8.6 Hz)	123.8	119.7
7	7.28 (t, 1H, 8.8 Hz)	7.22 (t, 1H, 8.6 Hz)	127.8	124.3
8	8.07 (d, 1H, 8.8 Hz)	7.69 (dd, 1H, 8.6, 2.3 Hz)	115.7	116.0
8a	–	–	123.3	120.6
9	–	–	175.1	181.4
9a	–	–	109.4	103.7
10	6.48 (d, 1H, 10.1 Hz)	6.77 (d, 1H, 10.3 Hz)	123.4	116.1
11	5.62 (d, 1H, 10.1 Hz)	5.62 (d, 1H, 10.3 Hz)	131.5	127.4
12	–	–	78.4	78.5
13	1.46 (s, 3H)	1.51 (s, 3H)	27.8	28.1
14	1.46 (s, 3H)	1.51 (s, 3H)	27.8	28.1
15	–	–	169.5	–
16	2.50 (s, 3H)	–	21.2	–
17	–	–	169.0	–
18	2.40 (s, 3H)	–	21.2	–
1’	–	–	41.7	41.4
2’	6.31 (dd, 1H, 17.4, 10.6 Hz)	6.69 (dd, 1H, 17.2, 10.3 Hz)	150.0	155.9
3’a	4.90 (d, 1H, 17.4 Hz)	5.22 (d, 1H, 17.2 Hz)	108.5	104.1
3’b	4.85 (d, 1H, 10.6 Hz)	5.06 (d, 1H, 10.3 Hz)	108.5	104.1
4’	1.70 (s, 3H)	1.64 (s, 3H)	29.9	28.4
5’	1.70 (s, 3H)	1.64 (s, 3H)	29.9	28.4
1-OH	–	13.43 (s, 1H)	–	–
5-OH	–	6.40 (s, 1H)	–	–

*Caloxanthone C (4).

for by the ^{1}H NMR spectrum which clearly shows that **11** has an acetyl instead of a hydroxyl group. The assignment was based on the absence of a downfield sharp singlet (δ 12.49) and an additional methyl group (δ 1.99) at high field region. Moreover, the FTIR analysis showed maximum absorption peaks of C-H stretching (2928 cm^{-1}), C=O group (1765 cm^{-1}), C=C aromatic stretching (1601 and 1435 cm^{-1}) and C-O group (1200 cm^{-1}) only. This analysis is in agreement with the observation of the disappearance of the OH group previously present in compound **8**.

Meanwhile, the ^{13}C NMR spectrum disclosed the presence of thirty carbon signals. The carbon signals were assigned by comparing with the ^{13}C NMR spectrum of compound **8**. The carbon signals resonated at δ 17.8 (C-25) , 20.8, 21.3 (C-27), 22.3 (C-18), 22.9 (C-22), 25.7 (C-26), 28.0 (C-14), 28.4 (C-28), 34.8 (C-15), 37.3 (C-17), 42.2 (C-21), 45.2 (C-19), 75.9 (C-16), 87.4 (C-20), 104.9 (C-2), 114.2 (C-6), 114.7 (C-4), 124.1 (C-23), 128.1 (C-10 and C-12), 129.3 (C-9 and C-13), 132.2 (C-24), 132.5 (C-11), 139.2 (C-8), 155.2 (C-5), 155.6 (C-3), 158.3 (C-1), 169.3 and 193.6 (C-7). Two remaining unidentified carbon signals were thus assigned as C-30 (δ 20.8) and C-29 (δ 169.3). The downfield signal was due to the carbonyl group. The analysis of the ^{1}H and ^{13}C NMR spectra concluded that the conversion of congestiflorone (**8**) to its acetate form was achieved. Table-2 summarizes the ^{1}H and ^{13}C NMR spectral data of congestiflorone acetate (**11**) and congestiflorone (**8**).

Conclusion

Further work on biological activities of chemical constituents isolated and their synthetic compounds will be established for their structure activity relationship.

ACKNOWLEDGEMENTS

Financial support from UPM under the RUGS research fund is gratefully acknowledged.

REFERENCES

1. T.J. Dennis and K.A. Kumar, *Fitoterapia*, **69**, 291 (1998).
2. W.M. Bandaranayak, S.S. Selliah and M.U.S. Sultanbawa, *Phytochemistry*, **14**, 265 (1975).
3. G.C.L. Ee, C.K. Lim, Y.L. Cheow and M.A. Sukari, *Malaysian J. Sci.*, **24**, 183 (2005).
4. G.C.L. Ee, C.K. Lim, G.P. Ong, M.A. Sukari and H.L. Lee, *J. Asian Nat. Prod. Res.*, **8**, 567 (2006).
5. T.R. Govindachari, B.R. Pai, P.S. Subramaniam, U.R. Rao and N. Muthukumaraswa, *Tetrahedron*, **23**, 243 (1967).
6. S. Walia and S.K. Mukerjee, *Phytochemistry*, **23**, 1816 (1984).
7. K. Awang, G. Chan, M. Litaudon, N.H. Ismail, M.T. Martin and F. Gueritte, *Bioorg. Med. Chem.*, **18**, 7873 (2010).
8. K.R. Bala and T.R. Seshadri, *Phytochemistry,* **10**, 1131 (1971).
9. C. Morel, D. Guilet, J.M. Oger, D. Seraphin, T. Sevenet, C. Wiart, A.H.A. Hadi, P. Richomme and J. Bruneton, *Phytochemistry*, **50**, 1243 (1999).
10. L. Verotta, E. Lovaglio, G. Vidari, P.V. Finzi, M.G. Neri, A. Raimondi, S. Parapini, D. Taramelli, A. Riva and E. Bombardelli, *Phytochemistry*, **65**, 2867 (2004).

TABLE-2
^{1}H NMR (500 MHz, $CDCl_3$) AND ^{13}C NMR (125 MHz, $CDCl_3$) DATA OF CONGESTIFLORONE ACETATE (**11**) AND CONGESTIFLORONE (**8**)

Position	^{1}H (δ)	*^{1}H (δ)	^{13}C (δ)	*^{13}C (δ)
1	–	–	158.3	164.7
2	6.29 (s, 1H)	6.09 (s, 1H)	104.9	98.7
3	–	–	155.6	163.5
4	–	–	114.7	107.6
5	–	–	155.2	158.4
6	–	–	114.2	105.6
7	–	–	193.6	199.2
8	–	–	139.2	142.0
9 & 13	7.79 (d, 2H, 7.5 Hz)	7.56 (d, 2H, 6.7 Hz)	129.3	128.0
11	7.50 (t, 1H, 7.5 Hz)	7.43 (t, 1H, 6.7 Hz)	132.5	130.6
10 & 12	7.39 (t, 2H, 7.5 Hz)	7.35 (t, 2H, 6.7 Hz)	128.1	127.4
14	2.87 (br s, 1H)	2.80 (br s, 1H)	28.0	27.4
15	2.05 (m, 2H)	1.96 (m, 2H)	34.8	34.8
16	–	–	75.9	76.0
17	1.94 (m, 2H)	1.60 (m, 2H)	37.3	37.5
18	1.31 (m, 2H)	1.25 (m, 2H)	22.3	22.0
19	2.05 (m, 1H)	2.05 (m, 1H)	45.2	44.6
20	–	–	87.4	87.7
21	1.94 (m, 2H)	1.73 (m, 2H)	42.2	42.0
22	2.22 (m, 2H)	2.15 (m, 2H)	22.9	22.9
23	5.16 (t, 1H, 6.9 Hz)	5.14 (t, 1H, 7.5 Hz)	124.1	124.0
24	–	–	132.2	132.2
25	2.00 (s, 3H)	1.64 (s, 3H)	17.8	17.8
26	2.00 (s, 3H)	1.70 (s, 3H)	25.7	25.8
27	1.00 (s, 3H)	1.04 (s, 3H)	21.3	21.4
28	0.79 (s, 3H)	0.74 (s, 3H)	28.4	27.7
29	–	–	169.3	–
30	1.99 (s, 3H)	–	20.8	–
1-OH	–	12.49 (s, 1H)	–	–

*Congestiflorone (8).

11. S.S. Teh, G.C.L. Ee, M. Rahmani, Y.H.T. Yap, R. Go and S.H. Mah, *Molecules*, **16**, 5647 (2011).
12. G.C.L. Ee, S.H. Mah, M. Rahmani, Y.H. Taufiq-Yap, S.S. Teh and Y.M. Lim, *J. Asian Nat. Prod. Res.*, **13**, 956 (2011).
13. M. Iinuma, H. Tosa, T. Tanaka and S. Yonemori, *Heterocycles*, **37**, 833 (1994).
14. M. Iinuma, H. Tosa, T. Tanaka and S. Yonemori, *Phytochemistry*, **35**, 527 (1994).
15. H.D. Locksley and I.G. Murray, *Phytochemistry*, **10**, 3179 (1971).
16. A.A.L. Mesquita, G. Oliveira and R.M.T. Neiva, *Phytochemistry*, **14**, 803 (1975).
17. G.C.L. Ee, S.S. Teh, H.C. Kwong, S.H. Mah, Y.M. Lim and M. Rahmani, *Phytochem. Lett.*, **5**, 545 (2012).
18. P. Yates and G.H. Stout, *J. Am. Chem. Soc.,* **80**, 1691 (1958).