Phytochemistry, Vol. 22, No. 3, pp. 792–794, 1983.
Printed in Great Britain.

0031 9422/83/030792-03$03.00/0
Pergamon Press Ltd.

COUMARINS OF *MURRAYA EXOTICA*—ABSOLUTE CONFIGURATION OF AURAPTENOL

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(*Revised received* 4 *August* 1982)

Key Word Index—*Murraya exotica*; Rutaceae; coumarins; auraptenol; absolute configuration; ^{13}C NMR spectra of auraptenol acetate; meranzin hydrate.

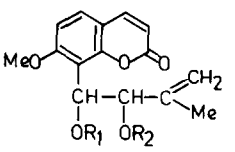
Abstract—3,5,6,7,3′,4′,5′-Heptamethoxyflavone, 3,5,6,8,3′,4′,5′-heptamethoxyflavone and murrangatin together with auraptenol and meranzin hydrate have been isolated from *Murraya exotica*. This is the first report of auraptenol and meranzin hydrate in this species and the first isolation of auraptenol from a natural source. The absolute configuration of auraptenol has been determined and found to possess *S* configuration at C-2′. The ^{13}C NMR spectrum of auraptenol acetate has been studied.

INTRODUCTION

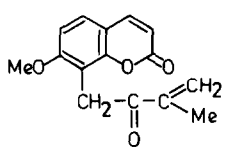
Several coumarins [1–5], carbazoles [6, 7] and flavonoids [8, 9] have been reported previously from *Murraya exotica* L. (Rutaceae). In the present investigation of the leaves of this species 3,5,6,7,3′,4′,5′-heptamethoxyflavone, 3,5,6,8,3′,4′,5′-heptamethoxyflavone (hibiscetin heptamethyl ether), murrangatin (**1**), auraptenol (**2**) and meranzin hydrate (**3**) were isolated. Auraptenol and meranzin hydrate are reported for the first time from this plant. The absolute configuration of auraptenol and its acetate including the ^{13}C NMR spectra are also established in the present communication.

RESULTS AND DISCUSSION

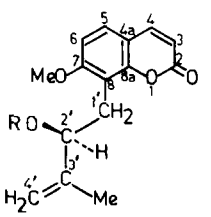
Auraptenol (**2**) showed the UV absorption characteristics of a coumarin. Strong absorptions at 3470 cm^{-1} (–OH) and 1690 cm^{-1} were indicative of a lactonic carbonyl, and 1600 cm^{-1} (aromatic nucleus) was discernible in the IR spectrum (KBr). The 80 MHz ^1H NMR spectrum ($CDCl_3$) displayed characteristic signals for a methyl group (δ1.82, 3H, *s*), an alcoholic hydroxyl function (δ2.10, 1H, *br* signal, disappeared on deuteration), a CH_2–CH-system (δ3.05, 2H, *m*; δ4.27, 1H, *m*), methoxyl group (δ3.86, 3H, *s*), exo-methylene group (δ4.76, 2H, *m*), two aromatic *ortho* protons (δ6.78 and 7.27, 1H, *d* each, J = 8.6 Hz) and the C-3 and C-4 protons of the coumarin nucleus (δ6.1 and 7.56, 1H, *d* each, J = 9.5 Hz). The secondary nature of the hydroxyl function (–CH–OH) was apparent from the downfield shift of the methine signal to δ5.42 in auraptenol acetate, $C_{15}H_{15}O_3$.OCOMe, mp 87–89°. All the above data closely resemble that of auraptenol isolated previously from Seville orange oil by Stanley *et al.* [10]. Subsequently, Dr. Stanley [personal communication] suggested that the auraptenol from this source was probably an artefact derived from the corresponding epoxide, meranzin ≡ auraptene (**4**). However, in our case, the presence of auraptenol in the crude petrol extract of the plant material (as evidenced from TLC) excluded the possibility of its being an artefact. Thus, the present isolation of auraptenol from *M. exotica* could be the first genuine isolation of this coumarin. The mass fragmentation pattern of auraptenol [*m/z* (rel. int.) 190 (100%), 189 (30.8), 175 (13), 161 (11.7), 160 (9.5), 131 (21.4) and 103 (5.4)] is also in conformity with the assigned structure (**2**). Further evidence in support of this structure has been



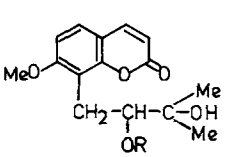
1 $R_1 = R_2 = H$
1a $R_1 = R_2 = Ac$



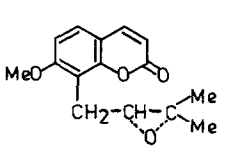
2b



2 R = H
2a R = Ac



3 R = H
3a R = Ac



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adduced by its conversion to the acetate derivative (**2a**) and by its oxidation to murrayone (**2b**). The absolute configuration of auraptenol bearing an asymmetric centre at the C-2′ position was established as *S* by Horeau's methods [11, 12].

Murrangatin (**1**) and meranzin hydrate (**3**) were eluted from the column with chloroform as a mixture which showed the presence of a hydroxyl group (broad, 3500 cm^{-1}) besides the usual coumarinic lactone. However, it was possible to resolve the mixture into two components on a Tswett column after acetylation because **1** formed a diacetate derivative (**1a**) and **3** formed a monoacetate derivative (**3a**). The UV absorption of the meranzin hydrate acetate (**3a**) showed the presence of a coumarin moiety and the IR spectrum indicated the presence of a hydroxyl, acetate carbonyl, lactone carbonyl and an aromatic nucleus. In the 90 MHz ^{1}H NMR spectrum ($CDCl_3$) characteristic signals were observed for two tertiary methyl groups (δ1.24 and 1.29, 3H, *s*, each), an alcoholic hydroxyl function (δ2.10, 1H, *br* signal, disappeared on deuteration), one acetate methyl group (δ2.10, 3H, *s*), a $-CH_2-CH-$system (δ3.16, 2H, *m*; δ5.02, 1H, *dd*, $J_1 = 9.2$ Hz, $J_2 = 3.3$ Hz), a methoxyl group (δ3.86, 3H, *s*), two aromatic *ortho* protons (δ6.75 and 7.26, 1H, *d* each, $J = 8.4$ Hz) and the C-3 and C-4 protons of the coumarin nucleus (δ6.15 and 7.55, 1H, *d* each, $J = 9.5$ Hz). The above data closely resemble those of meranzin hydrate acetate (**3a**) [13] reported by Kikuchi *et al.* As it was not possible to isolate meranzin hydrate itself, the absolute configuration of this coumarin at the C-2′ position could not be confirmed.

EXPERIMENTAL

The plant material was collected locally and verified by Dr. S. R. Das, Survey Officer, Regional Research Institute, Calcutta. A voucher specimen has been deposited at the Department of Chemistry, Calcutta University. Mps are uncorr. ^{1}H NMR (80 and 90 MHz) and ^{13}C NMR (20 MHz) spectra were recorded with TMS as an int. standard in $CDCl_3$. MS was operated at 15 eV. Si gel G (BDH, 60–120 mesh) and deactivated alumina (basic, Brockmann) were used for CC. Si gel G (Merck) was used for TLC. Samples were dried over P_2O_5 for 24 hr.

Isolation of auraptenol (**2**). Air-dried, powdered leaves of *Murraya exotica* L. (5 kg) were extracted with petrol in a Soxhlet apparatus. After the removal of solvent the crude material was chromatographed over deactivated alumina (basic). C_6H_6 and C_6H_6–$CHCl_3$ (1 : 3) eluate on trituration with a petrol–Me_2CO mixture gave a crystalline compound which on recrystallization from a petrol (40–60°)–Me_2CO (7 : 3) mixture afforded pure auraptenol (**2**) mp 105–107°; yield, 0.005%; $[\alpha]_D^{25}$ −11.83° ($CHCl_3$; *c* 1.01); +15.2° (EtOH; *c* 1.05). (Found: C, 69.48, H, 5.97; $C_{15}H_{16}O_4$ requires: C, 69.23, H, 6.15%.)

The crude material obtained from the $CHCl_3$ eluate was acetylated in the usual way with pyridine–Ac_2O and the product chromatographed over Si gel using a C_6H_6–EtOAc eluate (19 : 1) to give murrangatin diacetate (**1a**) (yield: 0.00102%), mp 127–129°, $[\alpha]_D^{25}$ +2.18° ($CHCl_3$; *c* 1.03) which was purified by recrystallization from petrol (40–60°) – Me_2CO (3 : 1) mixture: UV λ_{max}^{EtOH} nm (log ε): 321 (4.17), 258 (3.64), 248 (3.64); IR ν_{max}^{KBr} cm^{-1}: 1745 and 1245 (acetate carbonyl), 1725 (lactone carbonyl), 1610 (aromatic nucleus); 80 MHz ^{1}H NMR spectra ($CDCl_3$): δ 1.62 (3H, *s*, Me -3′), 1.99 (3H, *s*, OCOMe -2′), 2.01 (3H, *s*, OCOMe-1′), 3.94 (3H, *s*, –OMe), 4.80 (2H, *m*, $=CH_2$), 6.06 (1H, *d*, $J = 9$ Hz; H-2′), 6.7 (1H, *d*, $J = 9$ Hz, H-1′), 6.23 (1H, *d*, $J = 9$ Hz, H-3), 6.81 (1H, *d*, $J = 8.8$ Hz, H-6), 7.36 (1H, *d*, $J = 8.8$ Hz, H-5) and 7.56 (1H, *d*, $J = 9$ Hz, H-4). (Found: C, 63.90, H, 5.25; $C_{19}H_{20}O_7$ requires: C, 63.77, H, 5.55%.)

C_6H_6–EtOAc (7:3) eluate gave a solid which was crystallized from a petrol (40–60°)–Me_2CO (7 : 3) mixture to afford meranzin hydrate acetate (**3a**); yield: 0.002%; mp 139–140°; $[\alpha]_D^{25}$ +69° ($CHCl_3$; *c* 1.14). (Found: C, 63.47, H, 5.38; $C_{17}H_{20}O_6$ requires: C, 63.33, H, 5.55%.)

The C_6H_6–$CHCl_3$ (1 : 1) eluate from the column of deactivated alumina was rechromatographed over Si gel. $CHCl_3$ and 2% methanolic $CHCl_3$ eluates gave hibiscetin heptamethyl ether, $C_{16}H_{24}O_9$, mp 195–197° (from $CHCl_3$–Me_2CO). This was characterized by direct comparison (mmp, co-TLC and co-IR) with an authentic sample.

The C_6H_6–EtOAc (9:1–4:1) eluate from the deactivated alumina column was rechromatographed over Si gel. The C_6H_6–EtOAc (7:3) eluate afforded 3,5,6,7,3′,4′,5′-heptamethoxyflavone, $C_{16}H_{24}O_9$, mp 152–154° (from petrol–Me_2CO), which was also characterized by mmp, co-TLC and co-IR with an authentic sample.

Acetylation of aureptenol (**2**). Acetylation was carried out with pyridine–Ac_2O in the usual way and the product purified by chromatography over Si gel with C_6H_6 as eluate giving auraptenol acetate (**2a**); $C_{17}H_{18}O_5$; mp 87–89° [petrol (40–60°)–Me_2CO, 3:2]; $[\alpha]_D^{25}$ +52.85° ($CHCl_3$; *c* 0.98); IR ν_{max}^{KBr} cm^{-1}: 1740 and 1240 (acetate carbonyl), 1700 (lactone carbonyl), 1600 (aromatic nucleus); 80 MHz ^{1}H NMR spectrum ($CDCl_3$): δ1.85 (3H, *m*, Me-3′), 1.9 (3H, *s*, –OCOMe), 3.2 (2H, *m*, Ph–CH_2), 3.82 (3H, *s*, –OMe), 4.81 (2H, *m*, $=CH_2$), 5.47 (1H, *t*, $J = 6$ Hz, H-2′), 6.22 (1H, *d*, $J = 8.5$ Hz, H-3), 6.82 (1H, *d*, $J = 8$ Hz, H-6), 7.32 (1H, *d*, $J = 8$ Hz, H-5), 7.62 (1H, *d*, $J = 8.5$ Hz, H-4); ^{13}C NMR spectra ($CDCl_3$): δ170.0 (*s*, –OCOMe), 160.7 (*s*, C-2), 160.5 (*s*, C-8a), 143.0 (*d*, C-4), 142.8 (*s*, C-7), 127.0 (*d*, C-5), 113.8 (*s*, C-8), 112.8 (*d*, C-3), 112.5 (*s*, C-4a), 112.0 (*t*, C-4′), 107.0 (*d*, C-6), 78.0 (*s*, C-3′), 76.0 (*d*, C-2′), 55.8 (*q*, OMe), 26.2 (*t*, C-1′), 21.0 (*q*, –OCOMe), 18.0 (*q*, Me-3′); MS *m/z* (rel. int.): 302 $[M]^+$ (2.13), 260 (1.64), 242 (25.9), 211 (10.68), 190 (100), 189 (33.3), 175 (17.26), 161 (12.3), 131 (29.18), 103 (13.15), 77 (16.85). (Found: C, 67.39, H, 5.46; $C_{17}H_{18}O_5$ requires: C, 67.55, H, 5.29%.)

Oxidation of auraptenol (**2**). Oxidation of auraptenol (**2**, 40 mg) with MnO_2 in neutral conditions gave murrayone; $C_{15}H_{14}O_4$ (**2b**, 30 mg); mp 132–133° (petrol–C_6H_6, 1:1); UV λ_{max}^{EtOH} nm (log ε): 322 (4.17), 256 (3.67), 246 (3.69); IR ν_{max}^{KBr} cm^{-1}: 1725 and 1710 (aliphatic carbonyl and lactone carbonyl), 1600 (aromatic nucleus); 90 MHz ^{1}H NMR ($CDCl_3$): δ1.80 (3H, *s*, Me-3′), 3.74 (3H, *s*, –OMe), 4.24 (2H, *s*, Ph–CH_2), 5.78 (2H, *m*, $=CH_2$), 6.21 (1H, *d*, $J = 9$ Hz, H-3), 6.78 (1H, *d*, $J = 8.8$ Hz, H-6), 7.3 (1H, *d*, $J = 8.8$ Hz, H-5) and 7.70 (1H, *d*, $J = 9$ Hz, H-4). (Found: C, 69.33, H, 5.58; $C_{15}H_{14}O_4$ requires: C, 69.46, H, 5.42%.)

Reactions of auraptenol with racemic α-phenylbutyric anhydride (Horeau's method). Racemic α-phenylbutyric anhydride (400 mg) and auraptenol (100 mg) were dissolved in dry pyridine. The reaction mixture was left for 20 hr. The excess anhydride was decomposed by adding ice-cold H_2O (50 ml) and the aq. soln extracted with EtOAc (3 × 50 ml). The EtOAc extract was washed with 5% $NaHCO_3$ (3 × 40 ml) and H_2O and dried. The $NaHCO_3$ washings were washed with $CHCl_3$ to remove neutral matter and subsequently acidified with 10% HCl. The free acid liberated was extracted with $CHCl_3$ and worked-up in the usual manner. The free α-phenylbutyric acid was isolated from the $CHCl_3$ soln on evaporation. After drying the free acid recorded a rotation of $[\alpha]_D^{25} = -0.8°$.

Acknowledgements—We express our thanks to Sri. J. C. Ghosh and Sri. A. K. Acharya for spectral measurements and to Sri. S. Bhattacharya for technical assistance.

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Phytochemistry, Vol. 22, No. 3, pp. 794–795, 1983.
Printed in Great Britain.

0031-9422/83/030794-02$03.00/0

CARPUSIN: A NOVEL 2-HYDROXY-2-BENZYLCOUMARANONE FROM *PTEROCARPUS MARSUPIUM*

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(*Revised received* 12 *July* 1982)

Key Word Index—*Pterocarpus marsupium*; Leguminosae; heartwood; 2-hydroxy-2-benzylcoumaranone.

Abstract—The structure of carpusin, an extractive of the heartwood of *Pterocarpus marsupium*, has been established as 2-benzyl-2, 4', 6-trihydroxy-4-methoxybenzo(b)furan-3(2H)one, on the basis of spectral evidence and its conversion to tetra-*O*-methylmaesopsin and 4,6,4'-trimethoxyaurone.

In continuation of our earlier work [1] extraction of the heartwood of *Pterocarpus marsupium* and chromatography of the ether solubles over Si gel using chloroform–ethyl acetate (3:2) as eluent, afforded a colourless crystalline compound, $C_{16}H_{14}O_6$, mp 215°, $[\alpha]_D \pm 0°$, $M^{+\cdot}$ 302, designated as carpusin (**1a**).

Compound **1a** showed phenolic properties and gave a cherry-red colour with acetic anhydride and concentrated sulphuric acid characteristic of 2-hydroxy-2-benzylcoumaranones [2]. Functional analysis of **1a** showed a carbonyl (IR ν_{max} 1675 cm^{-1}), one phenolic methoxyl and one benzylic-CH_2- (^{1}H NMR 60 MHz singlets at δ 3.9