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MARMELINE, AN ALKALOID, AND OTHER COMPONENTS OF UNRIPE FRUITS OF *AEGLE MARMELOS*[*]

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Key Word Index—*Aegle marmelos*; Rutaceae; alkaloids; marmeline; aegeline; imperatorin; alloimperatorin; xanthotoxol.

Abstract—From unripe fruits of *Aegle marmelos*, a new alkaloid named marmeline was isolated and identified as *N*-2-hydroxy-2-[4-(3′,3′-dimethylallyloxy)phenyl]ethyl cinnamide. Aegeline, imperatorin, alloimperatorin and xanthotoxol were also present.

INTRODUCTION

In continuation of our studies on *Aegle marmelos* [1,2] examination of unripe fruits was undertaken. Isolation and characterization of a new cinnamamide alkaloid named marmeline is described. Aegeline, imperatorin, alloimperatorin and xanthotoxol were also isolated and identified.

RESULTS AND DISCUSSION

Acetone extracts of unripe fruit pulp of *A. marmelos* were subjected to column and preparative layer chromatography. The following constituents were isolated and characterized. Marmeline (**1**): mp 156–7°, M^+ 351, $C_{22}H_{25}O_3N$. Its UV absorption λ_{max} 216, 222, 273 nm (log ε 4.42, 4.41, 4.31), was characteristic of a *trans*-cinnamide structure and closely resembled aegeline and its ethers; IR further confirmed this observation [3, 4]. Its ^1H NMR spectrum showed a two proton doublet at δ 4.57, one proton triplet at δ 5.40 ($J = 7$ Hz), and two closely spaced 3 proton singlets at δ 1.72 and δ 1.74 due to *gem* diMe groups indicating the presence of a *γ,γ*-diMeallyloxy chain. Two olefinic protons of the cinnamoyl moiety were present as two doublets of one proton each at δ 6.73 and δ 7.56 ($J = 16$ Hz), while 5 aromatic protons were seen as a multiplet centred around δ 7.40. The aromatic region also showed two doublets of two protons each at δ 6.71 and δ 7.43 ($J = 9$ Hz) for A_2B_2 protons of a 1,4-disubstituted phenyl ring. An ABX pattern of the benzylic methine appeared as two sets of doublets centred at δ 4.78, shifted downfield to δ 5.97 on acetylation of the secondary OH group on the same carbon. A multiplet at δ 3.59 was assigned to methylene protons adjacent to the benzylic carbon. Marmeline was therefore formulated as *N*-2-hydroxy-2-[4-(3′,3′-dimethylallyloxy)phenyl]ethylcinnamamide (**1**). The structure was fully supported by the mass spectrum which showed the molecular ion at *m/z* 351 as a very small but clearly discernible peak; the base peak of the spectrum appeared at *m/z* 131 $[C_6H_5CH{=}CH{-}CO]^+$. Other prominent peaks appeared at *m/z* 333 ($M^+ - H_2O$), 282 $[M^+ - (CH_2CH{=}C(CH_3)_2]$, 264 ($333 - C_5H_9$), 202 (333 − 131), and 103 (131 − CO). IR, UV, NMR and MS of marmeline acetate (**2**) fully corroborated the assigned structure.

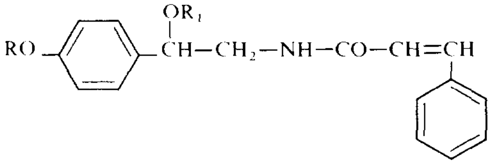
Marmeline is thus the parent compound of compound **3** isolated and characterized earlier [4]. In view of the easy artefact formation in the case of aegeline due to the alkylation of the OH group by alcohols during extraction [4] it could be reasonably derived that compound **3** might also have been an artefact; paucity of material did not permit confirmation.

Aegeline (**4**) isolated earlier from leaves [3] and the ripe fruit constituents imperatorin, alloimperatorin and xanthotoxol [2,5] were also isolated from unripe fruits and characterized.

EXPERIMENTAL

Mps are uncorr., UV spectra recorded in EtOH, IR in KBr discs and ^1H NMR with TMS (δ = 0) as int. standard. MS peaks, except the molecular and other ions of special significance, of rel. int. <6 % were not recorded.

Isolation. Coarsely powdered, unripe fruit pulp (1 kg) was extracted with Me_2CO. The concentrate was subjected to column chromatography followed by prep. TLC on Si gel to obtain TLC



1 $R = CH_2{-}CH\quad C(Me)_2$, $R_1 = H$
2 $R = CH_2{-}CH\quad C(Me)_2$, $R_1 = COMe$
3 $R = CH_2{-}CH\quad C(Me)$, $R_1 = Me$
4 $R = Me$, $R_1 = H$

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[*] Part III in the series "Constituents of *Aegle marmelos*". For part II see ref. [2].

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homogeneous components. These were identified by their UV, IR, ^{1}H NMR and MS and the known compounds were confirmed by direct comparison (TLC, mmp, IR) with authentic samples.

Identification. Marmeline (**1**), eluted with $CHCl_3$–Me_2CO (3:1); prep. TLC, $CHCl_3$–MeOH (9:1), R_f 0.74; TLC, C_6H_6–$CHCl_3$–EtOAc (8:1:1), R_f 0.32. Colourless, stout needles ($CHCl_3$–hexane) mp 156–7°, M^+ 351, $C_{22}H_{25}O_3N$; UV λ_{max} nm (log ε): 216 (4.42), 222 (4.41) 273 (4.31). IR ν_{max} cm^{-1}: 3340, 3255, 3080, 2925, 1730, 1725, 1648, 1620, 1578, 1570, 1565, 1560, 1513, 1505, 1445, 1381, 1352, 1234, 1200, 1170, 1060, 1010, 1005, 985, 890, 865, 830, 810, 760, 700. ^{1}H NMR (Me_2CO-d_6): δ 1.72, 1.74 (3H each, *s*, 2 × Me), 3.59 (2 H, *m*, CH_2–N), 4.57 (2 H, *d*, $J = 7$ Hz, OCH_2) 4.78 (1 H, *m*, CH–C), 5.40 (1 H, *t*, $J = 7$ Hz, –CH=C), 6.73, 7.56 (1 H each, *d*, $J = 16$ Hz, CH=CH–Ar), 6.71, 7.43 (2 H each, *d*, $J = 9$ Hz, A_2B_2–C_6H_4–), *ca* 7.40 (5 H, *m*, –C_6H_5). MS 70 eV, *m/z* (rel. int.): 351 (M^+ < 3), 333 (< 3), 265 (6), 264 (10), 203 (20), 164 (9), 163 (74), 162 (51), 161 (49), 160 (51), 159 (10), 149 (7), 148 (7), 144 (6), 143 (43), 137 (18), 136 (53), 133 (10), 132 (25), 131 (100), 124 (48), 123 (24), 121 (10), 115 (23), 103 (50), 96 (9), 86 (18), 85 (19), 78 (12), 77 (33), 69 (52).

Acetate (**2**). (Ac_2O pyridine). Colourless, long needles (EtOH–H_2O) mp 115–6°, M^+ 393, $C_{24}H_{27}O_4N$, UV λ_{max} nm (log ε): 219 (4.25), 225 (4.24), 276 (4.23). IR ν_{max} cm^{-1}: 3460, 3390 3080, 2930, 1765, 1755, 1662, 1650, 1620, 1610, 1573, 1550, 1510, 1370, 1337, 1230, 1175, 1020, 998, 968, 937, 870, 855, 825, 810, 760, 730. ^{1}H NMR ($CDCl_3$): δ 1.83, 1.87 (3 H each, *s*, 2 × Me) 2.17 (3 H, *s*, –OCOMe), 3.83 (2 H, *dd*, CH_2–N), 4.55 (2 H, *d*, $J = 7$ Hz, OCH_2–), 5.53 (1 H, *t*, $J = 7$ Hz, C=CH), 5.92 (1 H, *t*, CH–OAc), 6.37, 7.63 (1 H each, *d*, $J = 16$ Hz, $C\underline{H}=C\underline{H}$–Ar), 6.91, 7.34 (2 H each, *d*, $J = 9$ Hz, A_2B_2–C_6H_4–), *ca* 7.43 (5 H, *m*, C_6H_5). MS 70 eV *m/z* (rel. int.): 393 (M^+ < 3), 334 (< 3), 333 (3), 325 (6), 265 (23), 178 (13), 165 (58), 161 (17), 160 (6), 149 (9), 148 (6), 144 (13), 143 (100), 137 (10), 136 (8), 135 (12), 132 (7), 131 (55), 123 (26), 116 (7), 115 (51), 107 (6), 103 (19), 86 (11), 82 (6), 79 (10), 75 (12), 67 (52), 66 (20), 62 (13), 59 (9), 58 (9).

Aegeline (**4**). Eluted with $CHCl_3$–Me_2CO (3:1): prep. TLC, $CHCl_3$–MeOH (9:1), R_f 0.72; plates (EtOH), mp, mmp, 173–5°, M^+ 297, $C_{18}H_{19}O_3N$. UV, IR [3], ^{1}H NMR (Me_2CO-d_6): 2.73 (1 H, *bs*, OH eliminated with D_2O), 3.55 (2 H, *m*, –CH_2–N), 3.80 (3 H, *s*, OMe), 4.78 (1 H, *m*, CH–C), 6.75, 7.62 (1 H each, *d*, $J = 16$ Hz, CH=CH–Ar), 6.92, 7.42 (2 H each, *d*, $J = 9$ Hz, A_2B_2–C_6H_4), *ca* 7.50 (5 H, *m*, C_6H_5). Xanthotoxol, imperatorin, alloimperatorin [2,5].

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REFERENCES

1. Sharma, B. R., Rattan, R. K. and Sharma, P. (1980) *Indian J. Chem.* **19**, 162.
2. Sharma, B. R. and Sharma, P. (1981) *Planta Med.* (in press).
3. Chatterjee, A., Bose, S. and Srimany, S. K. (1959) *J. Org. Chem.* **24**, 687.
4. Manandhar, M. D., Shoeb, A., Kapil, R. S. and Popli, S. P. (1978) *Phytochemistry* **17**, 1814.
5. Saha, S. K. and Chatterjee, A. (1957) *J. Indian Chem. Soc.* **34**, 228.