

THREE NEW COUMARINS FROM MURRAYA EXOTICA

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Abstract — Three new coumarins named peroxyauraptanol (1) having hydroperoxy group, cis-dehydroosthol (3), and murraol (5) were isolated from leaves of Murraya exotica (Rutaceae), and the structures were assigned by chemical and/or spectro-metric studies.

During our investigation on the constituents of the plants of genus Murraya,¹ many kind of monomeric and dimeric carbazoles and coumarins have been isolated and determined the structures. This paper describes the isolation of three new coumarins, peroxyauraptanol, cis-dehydroosthol, and murraol from leaves of Murraya exotica L.,² and structure elucidation.

Peroxyauraptanol (1) was obtained (0.002% yield from fresh leaves) as colorless prisms, mp 114–116°C, $[\alpha]_D +3.53^\circ$ (CHCl₃). The molecular formula C₁₅H₁₆O₅ was suggested by analyses of chemical ionisation (CI) ms (NH₃ and iso-C₄H₁₀), ¹H-nmr, and ¹³C-nmr³ spectra. The presence of 7-methoxy-8-substituted coumarin nucleus in this molecule was indicated by the uv (MeOH) [λ_{max} 248, 257, and 322 nm], ir (CHCl₃) [ν_{max} 1730 cm⁻¹], and ¹H-nmr (CDCl₃) spectra [δ 3.95 (3H, s, OCH₃), 7.64 (1H, d, J = 9.4 Hz), 6.26 (1H, d, J = 9.4 Hz), 7.36 (1H, d, J = 8.7 Hz), and 6.87 (1H, d, J = 8.7 Hz)].⁴ Further, the ¹H-nmr spectrum showed ABC-type signals at δ 3.16 (1H, dd, J = 5.4 & 13.8 Hz), 3.27 (1H, dd, J = 7.7 & 13.8 Hz), and 4.60 (1H, dd, J = 5.4 & 7.7 Hz), two 1H-singlets at δ 4.88 and 4.94 assignable to exo-methylene protons, and a 3H-singlet at δ 1.91 due to an allyl methyl group. The appearance of the signals at δ_H 4.60 (1H, dd, J = 5.4 & 7.7 Hz), one of the ABC-type protons, and δ_C 87.3 (d) together with the occurrence of fragments corresponding to [M⁺•OH] and [M⁺•OOH] in the EI-ms spectrum, and ir band at 3520 cm⁻¹ showed the presence of hydroperoxy moiety in this coumarin. These data coupled with the observation of a significant mass fragment peak at m/z 189 (100

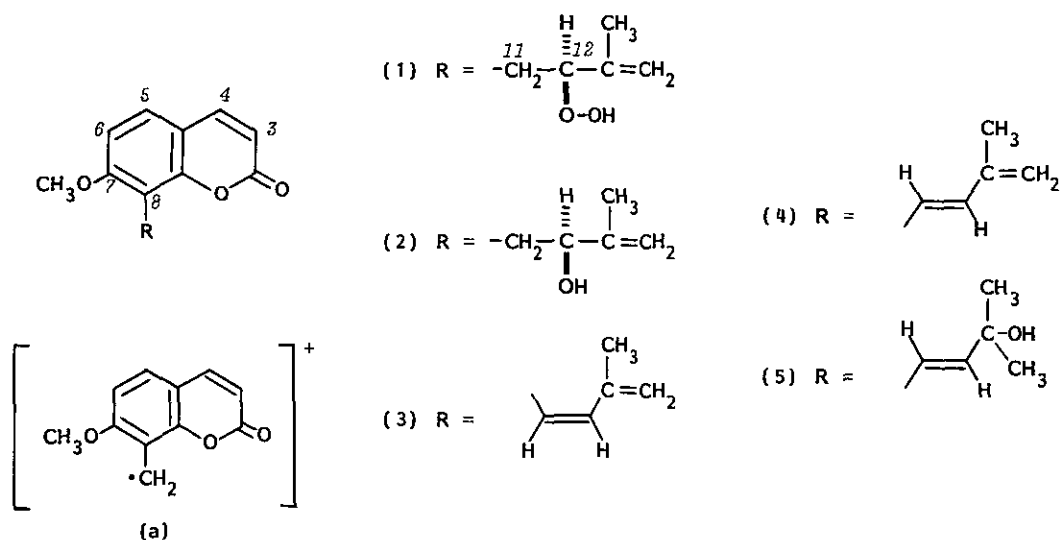
%) ascribed to an ion [a], showed the structure $[-CH_2-CH(OOH)-C(CH_3)=CH_2]$ for the side chain. Treatment of this coumarin with triphenyl phosphine in methanol at room temperature gave **2**: $[\alpha]_D -4.6^\circ$ ($CHCl_3$); 1H -nmr ($CDCl_3$) δ : 7.62 (1H, d, $J = 9.8$ Hz), 7.43 (1H, d, $J = 8.7$ Hz), 6.86 (1H, d, $J = 8.7$ Hz), 6.24 (1H, d, $J = 9.8$ Hz), 4.90 (1H, br s), 4.80 (1H, br s), 4.35 (1H, m), 3.93 (3H, s), 3.20 (dd, $J = 5.1$ & 13.8 Hz), 3.09 (1H, dd, $J = 13.8$ & 8.4 Hz), and 1.90 (3H, s); EI-ms m/z : 243 (M^+-17), 190 (100 %), 189, 175, 161, and 131; ir_{max} ($CHCl_3$) cm^{-1} : 1720 and 1610; $uv \lambda_{max}$ (MeOH) nm: 248, 257, and 322. All the above data were in agreement with those listed in the literature^{6,7} for auraptenol (**2**) which was first isolated from *Citrus aurantium*,⁶ and then, also from *M. exotica*⁷ collected in India. Negative $[\alpha]_D$ value in chloroform of **2** derived from peroxyauraptenol suggested S-configuration for the asymmetric center according to the proposition by Schoolery.⁷

These results led us to propose the structure **1** to peroxyauraptenol.

Since the first isolation of a coumarin hydroperoxide from the plants of genus *Mammea* by Crombie *et al.*,⁸ this is the second example of an isolation of hydroper-oxygenated coumarin from natural sources.

cis-Dehydroosthol (**3**), $C_{15}H_{14}O_3$ [m/z 242.0919 (M^+ , found); 242.0941, calcd.] was obtained (0.024% yield) as a colorless oil [ir_{max} ($CHCl_3$) cm^{-1} : 1725 and 1600] and gave uv spectral data typical of 7-oxygenated coumarin nucleus [$uv \lambda_{max}$ (MeOH) nm: 220, 277, and 322].⁴ The 1H -nmr ($CDCl_3$) spectrum contained signals assignable to a methoxy [δ 3.91 (3H, s)], an allyl methyl [δ 1.60 (3H, s)] and an exo-methylene group [δ 4.84 (2H, s)] as well as three pair of doublets [δ 7.62 (1H, d, $J = 9.4$ Hz), 7.36 (1H, d, $J = 8.7$ Hz), 6.84 (1H, d, $J = 8.7$ Hz), 6.45 (1H, d, $J = 12$ Hz), 6.24 (1H, d, $J = 9.4$ Hz), 6.20 (1H, d, $J = 12$ Hz)]. Among these three pair of doublets, two of them at δ 7.62 and 6.24, and δ 7.36 and 6.84 were easily assignable to H-4 and -3, and H-5 and -6, respectively, in coumarin nucleus.⁴

The observation of another pair of doublets having large coupling constant ($J = 12$ Hz) at δ 6.45 and 6.20 revealed the presence of (Z)-disubstituted double bond in the molecule. On the results of these spectral data coupled with a similar mass fragment pattern [m/z 242 (M^+ , 100%), 227, 211, 189, 183, 155, 131, 128, and 115] with that of trans-dehydroosthol (**4**)⁹ which was also isolated from the same plant source and characterized,¹⁰ the structure of cis-dehydroosthol was proposed to formula **3**.



Murraol (5), colorless prisms (0.013% yield), mp 105-107°C; $\text{C}_{15}\text{H}_{16}\text{O}_4$ [m/z 260.1029, found; 260.1047, calcd.]; uv λ_{max} (MeOH) nm: 244, 254, 274(sh.), 282, and 318; ir ν_{max} (CHCl_3) cm^{-1} : 1600, 1720, and 3450. The ^1H -nmr (CDCl_3) spectrum indicated the presence of a methoxy group [δ 3.95 (3H, s)] and two methyls [δ 1.47 (6H, s)] attached to a carbon atom bearing a hydroxy group [δ 1.82 (1H, broad s, exchangeable with D_2O)]. Observation of characteristic two pair of doublets [δ 7.62 and 6.26 (each 1H, d, $J = 9.4$ Hz), and δ 7.30 and 6.86 (each 1H, d, $J = 8.7$ Hz)]⁴ suggested that murraol possessed the same 7-methoxy-8-substituted coumarin nucleus as 1 and 3 described above. Remaining AB-type signals at δ 7.02 and 6.93 (each 1H, d) having a large coupling constant ($J = 16.4$ Hz) were attributable to (E)-disubstituted double bond same as that of trans-dehydroosthol (4). In the mass spectrum, murraol furnished ions at m/z 242 ($\text{M}^+ - \text{H}_2\text{O}$, 100%), 227, 211, 183, 155, 131, 128, and 115 corresponding to the behavior of 4, in addition to fragments at m/z 260 (M^+), 245, 218, 217, 203, and 189. Based on these results, we assigned structure 5 to murraol.

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- 2) Cultivated in Higashiyama Zoo & Botanical Garden, Nagoya.
- 3) 1: ^{13}C -nmr (CDCl_3) δ : 160.9 (s), 160.7 (s, C-2), 153.6 (s), 143.8 (d, C-4), 127.2 (d, C-5), 114.3 (s, C-8), 113.4 (t, C-14), 113.2 (d, C-3), 113.0 (s, C-9), 107.4 (d, C-6), 87.3 (d, C-12), 56.3 (q, OCH_3), 24.3 (t, C-11), and 18.6 (q, C-15); ms (EI) m/z 259, 190, 189, 175, 159, 146, 131, 118, and 103.
- 4) R. D. H. Murray, J. Mendez, and S. A. Brown, "The Natural Coumarins" p 27, John Wiley & Sons Ltd., New York, 1982.
- 5) Unfortunately, the yield of peroxyauraptanol (1) from the plant was so scarce that we could not obtain 2 enough to get the satisfactory $[\alpha]_D$ value [lit.⁷ $[\alpha]_D -11.83^\circ$ (CHCl_3)].
- 6) W. L. Stanley, A. C. Waiss, Jr., R. E. Lundin, and S. H. Vannier, Tetrahedron, **21**, 89 (1965).
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- 9) F. Bohlmann, H. Franke, and C. Zdero, An. Quim., **68**, 765 (1972).
- 10) 4: (0.004% yield) colorless oil; $\text{C}_{15}\text{H}_{14}\text{O}_3$ [m/z 242.0919 (M^+ , found); 242.0941, calcd.]; uv λ_{max} (MeOH) nm: 218, 262, 275, 290 (sh.), 300, 316, and 340 (sh.); ^1H -nmr δ (CDCl_3): 7.63 (1H, d, $J = 9.4$ Hz, H-4), 7.49 (1H, d, $J = 16.8$ Hz), 7.30 (1H, d, $J = 8.7$ Hz, H-5), 6.90 (1H, d, $J = 16.8$ Hz), 6.87 (1H, d, $J = 8.7$ Hz, H-6), 6.27 (1H, d, $J = 9.4$ Hz, H-3), 5.19 (1H, s, $=\text{CH}_2$), 5.14 (1H, s, $=\text{CH}_2$), 3.97 (3H, s, OCH_3), and 2.03 (3H, s, allyl- CH_3); ms m/z : 242 (M^+ , 100%), 227, 211, 183, 155, 131, 128, and 115.

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