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CONSTITUENTS OF THAI MEDICINAL PLANTS - III

NEW ROTENOID COMPOUNDS - STEMONACETAL, STEMONAL AND STEMONONE

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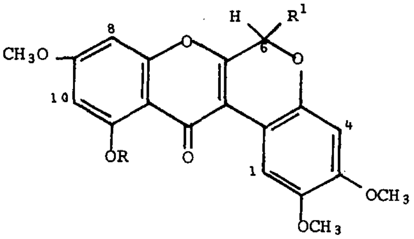
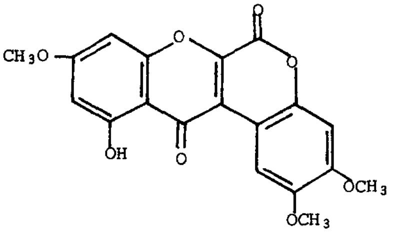
Four crystalline compounds have been isolated from the ethanol extracts of the ground dried roots of Stemona collinsae Craib.[1] The roots are reported[1b] to have insecticidal properties. Three of these, m.p. 203-204°, 215-216° and 229-230° are named stemonacetal, stemonal and stemonone respectively. This communication presents evidence for the structures of these new compounds as the rotenoids 1a, 1b and 2.

Stemonacetal, m.p. 203-204° has the formula $C_{21}H_{20}O_8$ from the elemental analytical figures[2] and the mass spectrum [M^+ at m/e 400 with a major ion at m/e 355 (M-45)]. The infrared spectrum (KBr) exhibits bands at 3400 (OH), 1650 (unsat. C=O), 1590, 1500, 1440, 1045, 1030, 875, 840, 800 and 790 cm^{-1}. λ_{max}^{EtOH} 275 nm (ε = 18,900); 303-320 nm (ε = 8,600). The compound gives positive tests for phenolic hydroxyl and carbonyl groups. The n.m.r. spectrum ($CDCl_3$) showed three methoxyl groups at δ 3.77, 3.83 and 3.91 (each 3H, s), an ethoxyl group (3.83, 2H, q and 1.20, 3H, t) and a phenolic OH (12.80, 1H, s, exch. D_2O). Aromatic singlets were present at 6.53 (1H, s, H_4), 8.33 (1H, s, H_1), 6.23 (2H, s, H_8 and H_{10}) and the acetal proton, H_6, appeared at 5.97 (1H, s). The n.m.r. values agree well with similar assignments in rotenoid compounds.[3-6]





1a R=H, R^1=OCH_2CH_3

1b R=H, R^1=OH

1c R=$COCH_3$, R^1=OCH_2CH_3

1d R=OCH_3, R^1=OCH_3

1e R=OCH_3, R^1=OCH_2CH_3

2

Acetylation of stemonacetal (1a) gave the acetate derivative (1c), $C_{23}H_{22}O_9$, m.p. 194-195°, with no hydroxyl absorption in its i.r. spectrum. ν_{max} (KBr) 1760 cm^{-1} (acetate). The n.m.r. spectrum ($CDCl_3$) showed signals at 2.45 (3H, s, CH_3CO), 3.91 (3H, s, OCH_3), 3.85 (6H, s, 2 x OCH_3), 1.22 (3H, t) and 3.85 (2H, q, OCH_2CH_3), 5.80 (1H, s, H_6), 6.57 (1H, s, H_4), 8.48 (1H, s, H_1), 6.57 (1H, d, J=2.2 Hz, H_8 or H_{10}) and 6.76 (1H, d, J=2.2 Hz, H_8 or H_{10}). In particular the coincidence of H_8 and H_{10} in stemonacetal is revealed in the acetate where their meta relationship is confirmed by the coupling constant.

Methylation of stemonacetal with dimethyl sulphate gave 1d, m.p. 206-207° with the molecular formula $C_{21}H_{20}O_8$ (M^+ at m/e 400). The n.m.r. spectrum ($CDCl_3$) showed resonances at 3.55 (3H, s, OCH_3), 3.82 (3H, s, OCH_3); 3.87 (3H, s, OCH_3) 3.93 (6H, s, 2 x OCH_3), 5.70 (1H, s, H_6), 6.62 (1H, s, H_4), 8.67 (1H, s, H_1), 6.32 (1H, d, J 2.2 Hz, H_8 or H_{10}) and 6.42 (1H, d, J 2.2 Hz, H_8 or H_{10})

When the methyl ether (1d) was heated in ethanol solution in the presence of p-toluenesulphonic acid compound (1e), $C_{22}H_{22}O_8$, m.p. 184° formed. M^+ at m/e 414 and major ion at m/e 369 (M-45). The n.m.r. spectrum ($CDCl_3$) showed resonances at 3.79 (3H, s, OCH_3), 3.85 (3H, s,OCH_3), 3.92 (6H, s, 2 x OCH_3), 1.21 (3H, t) and 3.83 (2H, q, OCH_2CH_3), 5.71 (1H, s, H_6), 6.5 (1H, s, H_4), 8.70 (1H, s, H_1), 6.23 (1H, d, J 2.2 Hz, H_8 or H_{10}) and 6.35 (1H, d, J 2.2 Hz, H_8 or H_{10}).

When the structures and spectral values of various rotenoids and related compounds are considered[3,4,5,6,7] the information described above leads to structure 1a for stemonacetal.

The other two compounds from S. collinsae are closely related and have been interconverted with stemonacetal. Stemonal, $C_{19}H_{16}O_8$, crystallises as yellow needles, m.p. 215-216°. M^+ at m/e 372. λ_{max}^{EtOH} 274 nm (ε = 16,300); 316 nm (ε = 7,500). ν_{max} (KBr) 3390 (OH), 1650 (unsat. C=O), 1610, 1590, 1480, 860, 800 and 760 cm^{-1}. It gives positive tests similar to those with stemonacetal. The n.m.r. spectrum [$(CD_3)_2SO$] showed signals at 4.09, 4.13, 4.18 (each 3H, s, OCH_3), 7.03 (1H, s, H_4), 8.62 (1H, s, H_1), 6.73 (1H, d, J 2.2 Hz, H_8 or H_{10}), 6.97 (1H, d, J 2.2 Hz, H_8 or H_{10}) and 13.1 (1H, s, phenolic OH). Structure 1b follows for stemonal since on treatment with ethanol and p-toluenesulphonic acid it is converted to stemonacetal (1a), m.p. 203°, as the only product. Similarly natural 1a yields the hemiacetal (1b) with aqueous acid. The reaction product in each case was identified by comparison of m.p., i.r., n.m.r. and mass spectra.

Stemonone, $C_{19}H_{14}O_8$, crystallises as orange needles, m.p. 229-230°. M^+ at m/e 370. ν_{max} (KBr) 3340 (OH), 1725 (lactone C=O), 1650 (unsat. C=O), 1590, 1570, 1460, 1030, 1020, 860, 825, 810, 792 cm^{-1}. λ_{max}^{EtOH} 274 nm (ε = 13,800); 298 nm (ε = 10,000); shoulder at 322 nm (ε = 6,300). Oxidation of stemonal (1b) with chromic oxide in the presence of acid gave a compound identical with stemonone, m.p. 228-230°, by mixed m.p., i.r. and mass spectra. Therefore stemonone has the structure 2.

Although the formation of stemonacetal from 1b is likely during the extraction procedure it appears that 1a is present in the plant. The synthesis of these rotenoid compounds is in progress.

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