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New norsesquiterpene aldehyde and sesquiterpene hemiacetal from the seed of *Polygonum hydropiper*

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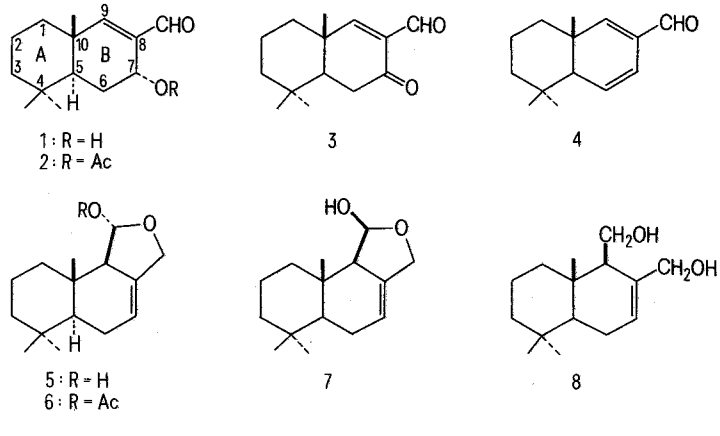
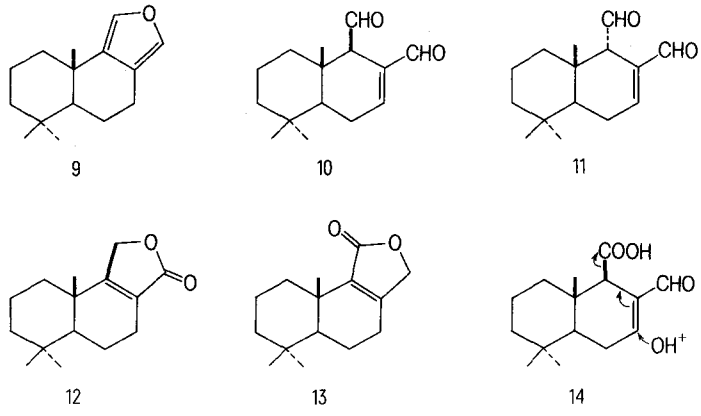
Summary. A new norsesquiterpene aldehyde, polygonal and a new sesquiterpene hemiacetal, isodrimeninol having drimane skeleton have been isolated from the seed of *Polygonum hydropiper,* and their structures have been established to be **1** and **5.** Polygonal showed pungency and plant growth inhibitory activity.

The leaf of the medicinal plant, *Polygonum hydropiper* (Polygonaceae), contains the intense pungent sesquiterpene, polygodial (**10**)[1,2]. The seed of this plant also shows the slightly different pungency from that of the leaf. We have now investigated the chemical constituents of the seed and a new norsesquiterpene aldehyde, polygonal (**1**) and a new sesquiterpene hemiacetal, isodrimeninol (**5**) have been isolated together with the previously known polygodial (**10**), isopolygodial (**11**) and confertifolin (**12**). Column chromatography and preparative TLC on silica gel of the crude extract of the ground seed of *P. hydropiper* resulted in the isolation of **1** (1.6%, total wight of the extract), **5** (2%), **10** (18%), **11** (5.5%) and **12** (2.2%).

Polygonal (**1**), $C_{14}H_{22}O_2$ (M^+ 222), m.p. 116–117 °C, $[\alpha]_D$ −7.3° (c, 7.4 in $CHCl_3$), showed the presence of an α,β-unsaturated aldehyde group [2740, 1675 cm^{-1}; 223 nm (log.ε, 4.14), 2,4-DNP, m.p. 139–140 °C; 370 nm (log.ε, 4.27)], a hydroxyl group (3400 cm^{-1}) and a double bond (1630 cm^{-1}). The NMR-spectrum contained the signals of three tertiary methyl groups (0.93, 1.00, 1.06 ppm, s, 9H), two of which might be gemdimethyl group (1385 and 1375 cm^{-1}), a vinylic proton (6.53 ppm, s) assignable to $-CH-C{=}CHO$ and a carbinyl proton (4.66 ppm, bs, $W_{1/2}$ = 7 Hz) and an aldehyde proton (9.50 ppm, s). The above spectral data, coupled with the molecular formula, showed that **1** was a bicyclic norsesquiterpene aldehyde with a hydroxyl group. The arrangement of B-ring of **1** is apparent from the following arguments. Acetylation of **1** with acetic anhydride-pyridine gave a monoacetate (**2**) [$C_{16}H_{24}O_3$ (M^+ − 60, 204); 1730, 1245 cm^{-1}; 2.00 ppm (s, 3H), 5.57 ppm (bs, $-CHOAc$)] and a small amount of dehydrated product (**4**) [$C_{14}H_{20}O$ (M^+ 204); 1683 cm^{-1}], indicating that **1** possessed a secondary alcohol. Oxidation of **1** with Collin's reagent afforded **3** [$C_{14}H_{20}O_2$ (M^+ 220); 10.03 ppm (s, CHO)]. The stereochemistry of the secondary hydroxyl group was confirmed to be α on the basis of the broad singlet ($W_{1/2}$ = 7 Hz) of H-7[3] and the facile formation of **4** from **1**. These results and the negative Cotton effect (235 nm, $\Delta\varepsilon$, −9.96; 330 nm, $\Delta\varepsilon$, −2.52), along with the co-occurrence of the other drimane type sesquiterpenes, **10,**





9 10 11

12 13 14

11 and **12,** and the biogenetic consideration (hydroxylation-decarboxylation) indicated in the formula **14,** show that the structure of polygonal is most favourably represented as the formula **1.** Polygonal has recently been afforded during the course of the synthesis of warburganal[4] and the spectral data of the natural polygonal were completely identical with those of the synthetic one[5].

Iso-Drimeninol (**5**), $C_{15}H_{24}O_2$ (M^+ 236), $[\alpha]_D$ −37° (c, 1.5), indicated the presence of a hydroxyl group (3400 cm^{-1}), 3 tertiary methyl groups (0.80, 0.86, 0.93 ppm, s, 9H), an isolated methylene group in an asymetrical environment attached to oxygen atom (4.15 and 4.50 ppm, d, J = 11 Hz), a carbinyl proton (5.26 ppm, d, J = 4 Hz) and a vinylic proton (5.50 ppm, bs). Reduction of **5** with $LiAlH_4$ gave a diol, m.p. 72–73 °C $[\alpha]_D$ −6.5° (c, 0.9), whose spectral data and physical constants were in accordance with drimane diol (**8**)[2,6,7], indicating that **5** possessed drimane skeleton with the same absolute configuration as polygodial (**10**).

Acetylation of **5** with acetic anhydride in pyridine afforded a monoacetate (**6**) ($[\alpha]_D$ −42.1° (c, 3.8); $C_{17}H_{26}O_3$ (M^+ 278); 1742, 1230 cm^{-1}; 2.02 ppm (s, 3H), together with a small amount of β,β-disubstituted furano compound (**9**) [$C_{15}H_{22}O$ (M^+ 218); 7.10 ppm (bs, 2H)][7,8]. The mild oxidation of **5** with Collin's reagent gave isodrimenin (**13**)[6]. The above chemical transformation showed that **5** was drimane type sesquiterpene hemiacetal with a hydroxyl group at C-11.

In fact, the IR-spectrum and the chemical properties of **5** were identical to those of drimeninol (**7**) which has been isolated from the liverwort[7]; however, their NMR-spectra and chromatographic behaviour was slightly different, conclusively establishing the structure **5** for isodrimeninol.

Polygonal (**1**) is the second pungent substance found in *P. hydropiper,* but its pungency is fairly weak in comparison with that of polygodial (**10**). Polygodial and polygonal completely inhibited the germination of the rice husk at ca. 100 and 500 ppm, respectively.

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Post mortem changes in adenylate cyclase activity in rat brain striatum

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Summary. Adenylate cyclase activity in rat striatum decreased post mortem. Half-lives were about 2.7 h at 22 °C, 72 h at 4 °C. Differences in stability after death of adenylate cyclase in human brain and rat striatum, and possible heterogenity of the enzyme, are briefly discussed.

There is strong evidence that cyclic AMP plays an important role in certain types of synaptic transmission, e.g. in catecholamine-mediated transmission. The properties of adenylate cyclase, the enzyme synthesizing cyclic AMP from ATP, have been investigated in brain tissue from, for example, rabbit, mouse, rat and monkey. There have been only a few and conflicting publications concerning adenylate cyclase in human brain: it was detected in slices of fresh surgery material, and its activity could be stimulated by various biogenic amines[2,3]. Activity of the enzyme was also detected in homogenates from various areas of human brain obtained 10 h after death; it was, however, not sensitive to catecholamines[4]. In contrast, Clément-Cormier et al.[5] could detect and stimulate the enzyme in homogenates of human striatum obtained 4 h after death.

Since the conflicting data could be the result of post mortem changes and since autopsy material is more readily available than surgical samples for the study of the human