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ORTHOSIPHON STAMINEUS AS A POTENT SOURCE OF METHYLRIPARIOCHROMENE A

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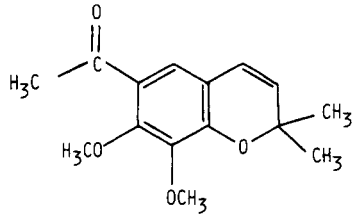
We have isolated methylriparіochromene A [**1**] or 6-(7,8-dimethoxy-2,2-dimethyl[2*H*,1-benzopyranne]-yl) ethanone from *Orthosiphon stamineus* Benth. (Labiatae) from Indonesia in high yield (4% of the dry matter).

Previously, this compound had been isolated from Compositae such as species of *Ageratina* (1) and *Eupatorium riparium* Regel (2,3) from the *Eupatorium* group or from the closely related *Stevia serrata* Cav. (4) and has been described as an oil. A structure based on nmr parameters was proposed by Kodha *et al.* (4).



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Having isolated this compound in its crystalline form, we were able to confirm its structure by means of an X-ray crystallographic study. This showed the existence of two planar molecules (A and B) in the asymmetric unit (Tables 1 and 2). Comparison of the geometric data of A and B (bond angles and lengths parameters, torsional angles) revealed some slight differences which can be imputed to weak interactions in the

TABLE 1. Coordinates for Nonhydrogen Atoms of Molecule A.

ATOM	*x*	*y*	*z*
O-1A	0.3640(3)	0.3781(1)	0.1331(1)
O-2A	0.4496(4)	0.1130(3)	0.0605(1)
O-3A	0.3846(3)	0.0180(3)	0.2102(1)
O-4A	0.3453(3)	0.2407(3)	0.2216(1)
C-1A	0.3829(4)	0.2679(3)	0.1264(2)
C-2A	0.3752(4)	0.1997(4)	0.1711(2)
C-3A	0.4033(4)	0.0877(4)	0.1668(2)
C-4A	0.4394(4)	0.0431(3)	0.1165(2)
C-5A	0.4430(5)	0.1140(4)	0.0710(2)
C-6A	0.4175(4)	0.2251(4)	0.0757(2)
C-7A	0.4246(5)	0.3020(4)	0.0303(2)
C-8A	0.3798(5)	0.4034(4)	0.0348(2)
C-9A	0.3098(5)	0.4418(4)	0.0849(2)
C-10A	0.1516(6)	0.4254(5)	0.0783(2)
C-11A	0.3499(6)	0.5590(4)	0.0994(2)
C-12A	0.4690(5)	−0.0759(4)	0.1067(2)
C-13A	0.5224(6)	−0.1503(4)	0.1513(2)
C-14A	0.4779(7)	0.0351(5)	0.2581(2)
C-15A	0.2113(6)	0.2901(5)	0.2253(2)

TABLE 2. Coordinates for Nonhydrogen Atoms of Molecule B.

ATOM	x	y	z
O-1B	0.1134(4)	0.1072(3)	0.8605(1)
O-2B	0.1899(4)	0.3572(3)	0.9716(1)
O-3B	0.1493(3)	−0.2677(2)	0.8085(1)
O-4B	0.1148(4)	−0.0511(3)	0.7805(1)
C-1B	0.1332(5)	−0.0004(4)	0.8758(2)
C-2B	0.1340(5)	−0.0799(4)	0.8349(2)
C-3B	0.1920(4)	−0.1886(4)	0.8489(2)
C-4B	0.1817(4)	−0.2202(4)	0.9039(2)
C-5B	0.1804(5)	−0.1378(4)	0.9438(2)
C-6B	0.1573(5)	−0.0296(4)	0.9309(2)
C-7B	0.1535(6)	0.0588(5)	0.9709(2)
C-8B	0.1130(6)	0.1570(5)	0.9570(2)
C-9B	0.0522(6)	0.1809(4)	0.9006(2)
C-10B	−0.1055(6)	0.1627(5)	0.8963(2)
C-11B	0.0880(8)	0.2938(5)	0.8811(3)
C-12B	0.2078(6)	−0.3360(4)	0.9240(2)
C-13B	0.2572(6)	−0.4231(4)	0.8869(2)
C-14B	0.2553(5)	−0.2638(4)	0.7698(2)
C-15B	−0.0230(7)	−0.147(5)	0.7627(2)

elementary lattice which are in no way significant.

EXPERIMENTAL

PLANT MATERIAL.—*O. stamineus* was supplied by Vitaflor, Quétigny-les-Dijon, France; a voucher specimen is preserved in the Laboratoire de Botanique et Cryptogamie, Nantes.

EXTRACTION.—Dried flower tops and leaves (100 g) of *O. stamineus* were extracted with EtOH at room temperature over 48 h. The concentrated gum was dissolved in Et_2O. The organic phase was then washed with NaCl-saturated H_2O, dried over Na_2SO_4, and evaporated. Two successive cc's of the resulting oil on Merck SiO_2 Art 7734 (eluent Et_2O) afforded 4 g of pure 6-(7,8-dimethoxy-2,2-dimethyl[2*H*,1-benzopyranne]-yl) ethanone as a yellowish oil that spontaneously gave crystals after resting in the dark at room temperature (mp 35°).

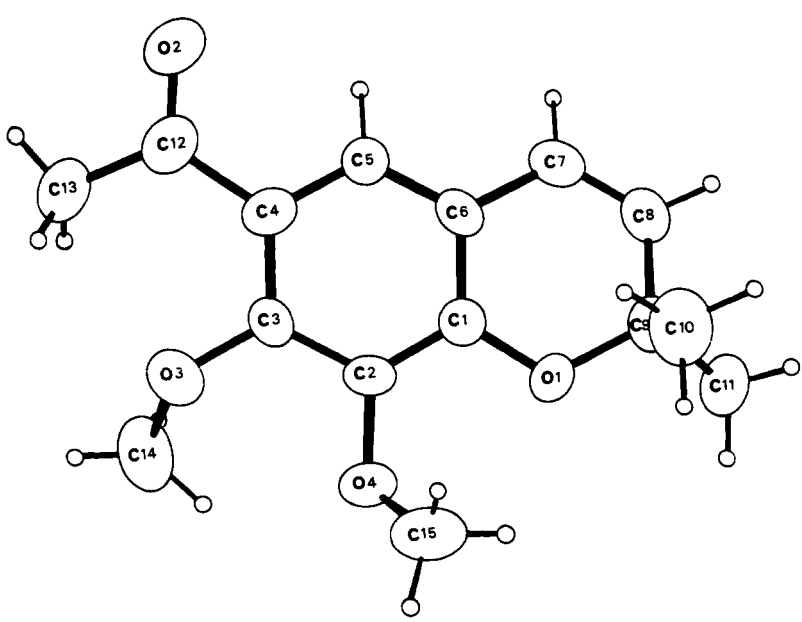

FIGURE 1. The molecular structure of methylripariochromene A [**1**].

X-RAY DATA.[1]—A yellowish crystal of methylripariochromene A, $C_{15}H_{18}O_2$, dimensions 0.30 × 0.30 × 0.20 mm, was selected. All measurements were carried out an Enraf-Nonius CAD-4 diffractometer system using MoKα radiation (λ = 0.71073 Å) with an ω/2θ scan technique (Θ max = 26°). Unit cell parameters were determined by least-squares fit of 25 reflections, which yielded a = 9.469(3), b = 12.132(4), c = 24.448(6) Å, α = γ = 90°, β = 93.99(4)°, and V = 2801.5(5) Å^3. For Z = 8 the computed density was 1.24 g/cm^3. Examination of systematic extinction indicated that the monoclinic crystal belonged to the space group $P2_1$ and that two molecules formed the asymmetric unit. Data collection gave 2532 independent reflections with $I > \sigma(I)$.

The structure was resolved using a MULTAN 80 method with the Enraf-Nonius SPD programs (5–8). The best solution revealed all nonhydrogen atoms of the two molecules of the asymmetric unit. After isotropic and anisotropic refinements, a difference Fourier plot showed the hydrogen atoms between the densities of 0.34 and 0.17 Å. The best refinement by a full matrix least-squares method gave R = 0.053, R_w = 0.052, and S = 1.43 for 452 refined parameters.

[1]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

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