

STILBENOLIGNAN FROM *MAACKIA AMURENSIS*

N. I. KULESH,* V. A. DENISENKO and O. B. MAKSIMOV

Pacific Institute of Bioorganic Chemistry, Far East Division of Russian Academy of Sciences, 690022 Vladivostok, Russia

(Received in revised form 27 February 1995)

Key Word Index—*Maackia amurensis*; Leguminosae; heartwood; stilbene; stilbenolignane; maackoline; gnetifolin.

Abstract—A novel stilbenolignan, named maackoline has been obtained from heartwood of *Maackia amurensis*. Its structure was established as 7-epi,8'-epi,11-de-O-methyl-5'-methoxygnetifolin F on the basis of spectral data.

INTRODUCTION

Maackia amurensis Rupr. et Maxim. is a tree widely distributed in southern part of the Russian Far East as well as in Mandshuria and Korea. Takai *et al.* [1] were the first to have investigated the phenolic constituents of the Japanese variety of this species (var. *buergeri* (Maxim.) C.K. Schneid). In an ethanol extract of heartwood they found the isoflavones, formononetin, genistein and 4',7-dihydroxy-3'-methoxyisoflavone, and two pterocarpanes, maackiain and medicagol. We have investigated the components of *M. amurensis* growing in Russian territory in the vicinity of the northern boundary of this species. In an ethanol extract of heartwood we detected four isoflavones, formononetin, genistein, retusin [2] and afromosin [3], two stilbenes, resveratrol and piceatannol, and isoflavonostilbene (3) (named maackiasine)—the first representative of a new type of naturally occurring polyphenol [2, 4]. Pterocarpanes were not detected in the sample of heartwood investigated.

Recently, from a more polar fraction of the ethyl acetate soluble part, of the ethanol extract we isolated two previously known dimeric stilbenes, scirpusin A (4) and scirpusin B (5), and a new dimeric compound maackin (6) with dioxane-type bound monomeric stilbene moieties [5].

The present paper describes the isolation and structural determination for a novel stilbenolignane 1. Its structure was suggested on the basis of spectral data and was similar to that of gnetifolin F from *Gnetum parvifolium* [6].

RESULTS AND DISCUSSION

Compound 1 showed no optical activity. Its EI-mass spectrum exhibited a prominent $[M]^+$ at m/z 452 and an

ion at m/z 244, indicating the presence of a stilbene moiety. UV spectra suggested the absence of 1 of the highly conjugated system, which is characteristic of dimeric stilbenes. Acetylation yielded the pentaacetyl derivative 2, indicating the presence of five hydroxy groups in 1. The structure 2 was elucidated by NMR (1H and ^{13}C), a series of selective decoupling experiments and difference spectra (NOE, INDOR), as well as the ^{13}C NMR proton-coupled spectrum.

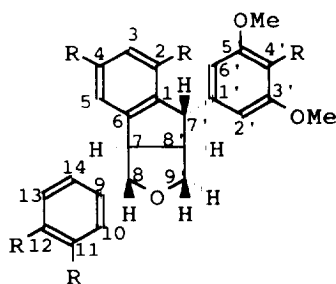
Significant differences in the 1H NMR spectra of the pentaacetyl derivative of maackoline and the tetraacetyl derivative of gnetifolin F [3] were observed only for proton signals belonging to the aromatic substituents at C-8 and C-7'. This suggests the presence of the same 3-oxabicyclo-[3,3,0]-octane moiety in the two molecules. However, NOE-difference experiments showed that in maackoline there is probably a *trans*-relationship between H-7 and H-8, as well as between H-7' and H-8', and *cis* relationship between H-7 and H-8'. The existence of NOE between the H-8 and H-7' protons is in a good agreement with this assumption. The *trans*-relationship between H-7' and H-8' was confirmed also by the value of $J_{7,8}$ (1.8 Hz) in the spectrum of maackoline (1). This observation showed that the value of the (H-7')-C-C-(H-8') dihedral angle is near 90° . A molecular model study proved that such a situation is possible only if there is *trans* relationship between H-7' and H-8'. As a result, the structure of maackoline (1) must be assigned as 7-epi,8'-epi,11-de-O-methyl-5'-methoxygnetifolin F.

EXPERIMENTAL

IR were measured in KBr. NMR were recorded at 250 MHz for 1H and 63 MHz for ^{13}C , in $CDCl_3$ and acetone- d_6 solns, using TMS as int. standard. UV were measured in MeOH.

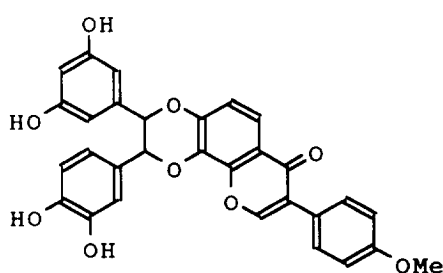
The tree was cut down (March, 1992) in the neighbourhood of Vladivostok (Primorye District, Russia). Heartwood sawdust was extracted with 95% EtOH for 24 hr at

*Author to whom correspondence should be addressed.

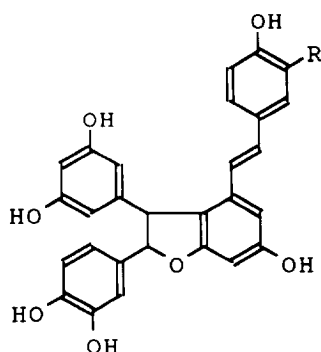


1: R=H;

2: R=Ac

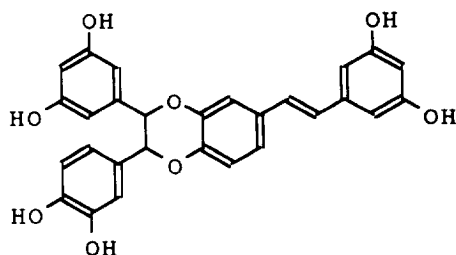


3



4: R=H;

5: R=OH



6

Table 1. Chemical shifts (ppm) and spin coupling constants (Hz)* in ^1H and ^{13}C NMR spectra of compounds 1 and 2

H-atom	Compound		C-atom	Compound	
	1	2		1	2
4	6.28 <i>d</i> , 2.2	6.77 <i>d</i> , 2.2	1	147.5	147.4
6	6.35 <i>d</i> , 2.2	6.90 <i>d</i> , 2.2	2	135.1	140.3
7	3.78 <i>dd</i> , 8.4; 4.5	3.85 <i>dd</i> , 9.0; 6.1	3	158.9	152.2
8	4.67 <i>d</i> , 4.5	4.84 <i>d</i> , 6.1	4	102.1	115.6
10	6.93 <i>d</i> , 1.8	7.23 <i>d</i> , 2.1	5	154.9	151.0
13	6.82 <i>d</i> , 8.2	7.22 <i>d</i> , 8.3	6	102.7	115.6
14	6.78 <i>dd</i> , 1.8; 8.2	7.30 <i>dd</i> , 2.1; 8.3	7	58.9	59.3
2', 6'	6.40 <i>s</i>	6.32 <i>s</i>	8	87.4	85.4
7'	4.18 <i>d</i> , 1.8	4.27 <i>d</i> , 6.0	9	136.3	141.4
8'	3.04 <i>dq</i> , 3 \times 8.4; 1.8	3.33 <i>m</i> , 4.6; 6.0; 6.7; 9.0	10	113.4	120.8
9' _{ax}	3.49 <i>t</i> , 2 \times 8.4	3.97 <i>dd</i> , 9.2; 4.6	11	145.0	142.1
9' _{eq}	4.43 <i>t</i> , 2 \times 8.4	4.37 <i>dd</i> , 9.2; 6.7	12	144.2	141.4
2 \times OMe	3.71 <i>s</i>	3.75 <i>s</i>	13	115.1	123.5
OH	6.96 <i>s</i>		14	117.7	123.4
2 \times OH	7.89 <i>bs</i>		1'	134.6	133.3
OH	8.23 <i>bs</i>		2', 6'	105.5	101.4
OAc		<i>s</i> 1.77; 2.29; 2.30; 2.30; 2.32	3', 5'	147.7	145.9
			4'	121.9	127.0
			7'	51.0	54.9
			8'	55.3	57.3
			9'	73.6	73.3

*Solvent: 1 acetone- d_6 ; 2— CDCl_3 , int. std. TMC. ^{13}C NMR, signals for acetyl groups appeared at 20.0, 20.3, 20.5, 21.0 ppm (CH_3), and 167.7, 167.8, 168.3 ppm ($\text{C}=\text{O}$), as well as a OMe signal at 56.2 ppm.

50° (× 3). The combined and concd extracts were successively re-extracted with hexane and EtOAc. The EtOAc fr. was sep'd on a silica gel eluted column, with a MeOH-CHCl₃ gradient. Rechromatography of a fr. obtained from silica gel and Sephadex LH-20 columns with various solvent systems gave the pure stilbenolignan **1** as a cream-coloured amorphous powder. (Found: C, 67.37; H, 5.70. C₂₅H₂₄O₈ required: C, 66.35; H, 5.35). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 285. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1112, 1280, 1462, 1518, 1616, 2485, 2938, 3400 (*br*). EIMS *m/z*: 452 [M]⁺, 422, 358, 344, 328, 314, 300, 284, 270, 256, 244, 167, 137, 107. **Pentaacetate 2**. Colourless crystals, mp 90–92°. (Found: C, 61.83; H, 5.57. C₃₅H₃₄O₁₃ required: C, 63.42; H, 5.17). EIMS *m/z*: 662 [M]⁺, 620, 536, 398, 314, 300, 218, 148, 102, 86, 43.

REFERENCES

1. Takai, M., Yamaguchi, H., Saitoh, T. and Shibata, S. (1972) *Chem. Pharm. Bull.* **20**, 2488.
2. Maksimov, O. B., Krivoshchekova, O. E., Stepanenko, L. S. and Boguslavskaya, L. V. (1985) *Khim. Prirodn. Soed.* **6**, 775.
3. Maksimov, O. B., Kulesh, N. I. and Gorovoy, P. G. (1992) *Rastit. Resursy* **28**, 157.
4. Krivoshchekova, O. E., Stepanenko, L. S. and Maksimov, O. B. (1986) *Khim. Prirodn. Soed.* **1**, 39.
5. Kulesh, N. I., Isakov, V. V. and Maksimov, O. B. (1992) *Khim. Prirodn. Soed.* **1**, 468.
6. Lin, M., Li, J. B., Wu, B. and Zheng, O. T. (1991) *Phytochemistry* **30**, 4201.