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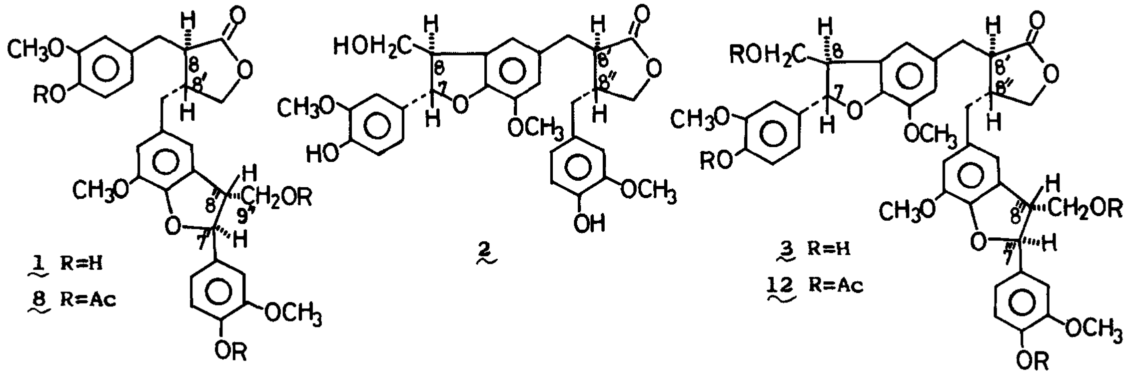
STEREOCHEMISTRY OF LAPPAOL A AND F

Akitami Ichihara*, Yasuji Nakamura, Hirokazu Kawagishi, and Sadao Sakamura
Department of Agricultural Chemistry, Faculty of Agriculture
Hokkaido University, Sapporo 060, Japan

Summary. The absolute configuration of lappaol A and F was determined by the correlation of the ozonolysis products with 2R,3R-(-)-dicarbomethoxymethyl-γ-butyrolactone and S-(-)-methyl paraconate.

In the previous papers, we reported the structural determination of lappaol A (1)[1)] and lappaol F (3)[2)], which are belong to typical sesquilignan[1)] and dilignan[2)] respectively. In this communication, we would like to describe further investigation on the absolute configuration of these compounds, and lappaol A and F were proved to be depicted as 1 (isolappaol A 2)[3)] and 3 respectively.

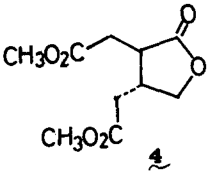


1 R=H
8 R=Ac

2

3 R=H
12 R=Ac

Stereochemistry of Lappaol A (1): Ozonolysis of 1 and treatment with 3% methanolic HCl yielded a lactone 4, $[\alpha]_D^{20}$ + 21.3° (C=0.80, CH_3OH). On the other hand, ozonolysis of arctigenin (5), whose absolute configuration was unequivocally established,[4)] gave the same lactone 4, $[\alpha]_D^{20}$ + 21.4 (C=1.04, CH_3OH). This result indicates that the lactone moiety in 1 has 8-R, 8'-R configuration (8'-R, 8"-R configuration in 2). As for the dihydrobenzofuran moiety in 1, the stereochemistry was confirmed as follows. Hydrogenation of 1 with Pd-C gave a hydrogenolized product 6, which was oxidized with ozone and then treated with 3% methanolic HCl to yield paraconic acid methyl ester, 7, $[\alpha]_D^{20}$ - 30.0° (C=1.1, CH_3OH). Since optically active methyl



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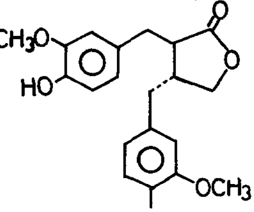

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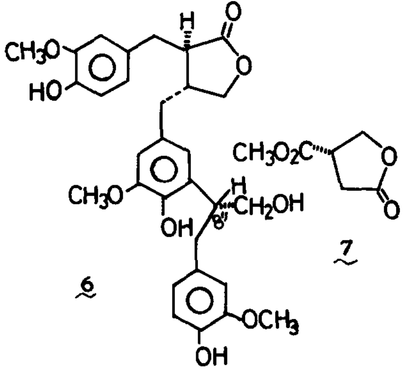
paraconate 7, $[\alpha]_D^{20}$ - 31.8° was known,[5] the absolute configuration at C-8'' should be depicted as 1. The relative configuration of C-8'' and C-7'' was deduced from comparison of the PMR spectra with compounds possessing known configuration (Table). Thus, it was known that the methyl signals in cis-2-aryl-3-methyl-2,3-dihydrobenzofuran shift to higher field in a range of 0.4~0.6 ppm compared with those of trans isomers.[6] However no such a shift was observed with the C-9'' methylene signals of lappaol A triacetate (8) compared with those of dehydrodiconiferyl alcohol acetates 9 and 10, which have trans-configuration. In conclusion, total stereostructures of lappaol A and isolappaol A were confirmed to be 1 and 2 respectively.



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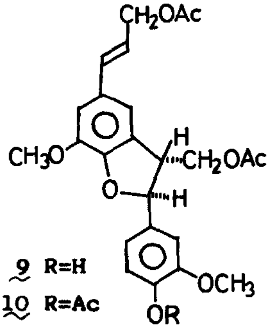

9 R=H
10 R=Ac

Table. PMR spectra with the dihydrobenzofuran moiety ($\delta^{CDCl_3}_{TMS}$)

	$-CH_2OAc$	-CHO-
8	4.38	5.52, J=6Hz
12	4.39	5.49, J=7Hz
9	4.48	5.56, J=7Hz
10	4.35	5.49, J=6Hz

Stereochemistry of Lappaol F (3): Ozonolysis and subsequent treatment with 3% methanolic HCl of 3 gave the butyrolactone 4, $[\alpha]_D^{20}$ + 20.0° (C=1.5, CH_3OH). Hydrogenolysis of 3 on Pd-C yielded a product which subjected to ozonolysis and treatment of methanolic HCl to give methyl paraconate 7, $[\alpha]_D^{20}$ - 33.9° (C=0.69, CH_3OH). The relative configuration at C-7 and C-7''' was deduced by the same way described above (Table), and the absolute configuration 3 was deduced.

References and Notes

1) A. Ichihara, K. Oda, Y. Numata, S. Sakamura, Tetrahedron Lett., 3961 (1976).
2) A. Ichihara, S. Kanai, Y. Nakamura, S. Sakamura, Tetrahedron Lett., 3035 (1978).
3) It has been clarified that 1 and 2 were obtained as a mixture (3 : 2). A. Ichihara, N. Nio, Y. Terayama, R. Kimura, S. Sakamura, preceding paper.
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