THE STRUCTURE OF NEW LIGNAN, LAPPAOLS

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New classes of lignan, lappaols were isolated from seeds of Arctium lappa L. Lappaol A(1), B(2), C(3), D(4), E(5), isolappaol A(6), isolappaol C(7) were termed as "sesquilignan", since these compounds were constructed from three units of coniferyl alcohol (one and a half of that of usual lignan). The structural elucidation was performed by spectroscopic analysis of these compounds and the derivatives obtained by acetylation, methylation and acid treatment. For examples, the structure of 1 was determined as 2-(3-methoxy-4-hydroxy)benzyl-3-[2-(3-methoxy-4-hydroxy)phenyl-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl] methyl-butyrolactone, and further confirmed by the synthesis of dehydrolappaol A dimethyl ether (8) via Michael addition of 2-(3,4-dimethoxyphenyl)-3-methyl-5-(dimethylthio-1-yl)-7-methoxy benzo [b] furan to 2-(3,4-dimethoxybenzyl)-γ-crotonolactone. Lappaol F(9), G(10), H(11), I(12) and J(13) were tetramers of coniferyl alcohol and should be called as "dilignan". The structure of 9 was deduced to be 2-[2-(3-methoxy-4-hydroxy)phenyl-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl] methyl-3-[2-(3-methoxy-4-hydroxy)phenyl-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl]methyl-butyrolactone.

Ozonigation of 1, decomposition of the ozonide and subsequent treatment of the oxidation product with methanolic HCl yielded (2R,3R)-2,3 dicarbomethoxymethyl-butyrolactone, $[\alpha]_D^{20}$ + 15.6 (C=1.8, CH_3OH), whose optical rotation was almost identical with the lactone, $[\alpha]_D^{20}$ + 15.0 (C=3, CH_3OH), derived from arctigenin by the same treatment. Further ozonization and, methanolic HCl treatment of the hydrogenolysis product of 1 gave (+)-paraconic acid methyl ester, $[\alpha]_D^{20}$ + 32.0. Since the relative configuration on the dihydrobenzofuran moiety was deduced to be trans on the basis of the PMR spectrum, whole stereostructure of 1 was elucidated to be (2R,3R)-2-(3-methoxy-4-hydroxy)benzyl-3-[(2R,3S)-2-(3-methoxy-4-hydroxy) phenyl-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl] methyl-butyrolactone.