ULMOPRENOL, A NEW TYPE C₃₀-POLYPRENOID FROM EUCOMMIA ULMOIDES, OLIVER

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Various polyprenoids have been characterized from mammalians, insects, plants, and fungi¹⁾. Most of them have the same α -terminal as shown in I and some of them have ambiguity as to the precise configuration of the olefinic bonds^{1a)}. In this communication, we wish to describe the isolation and structure elucidation of ulmoprenol(II), a new C₃₀-polyprenoid with a novel α -terminal, from Eucommia ulmoides Oliver (Tu-Chung), that is one of the oldest tonic herbs in China²⁾.

Ulmoprenol(II), bp.180-185°/5×10⁻⁵Torr, $[\alpha]_D^{20}$ =-15°, was isolated from an ethanol extract of Tu-Chung bark by means of combination of column and preparative thin layer chromatography³⁾. The structure II is here presented for this compound on the basis of the following spectral and chemical evidences.



The molecular formula of II $(C_{30}H_{50}O)$ was supported by elemental analysis and MS (M⁺ 426.3889, calcd 426.3859). The IR spectrum of II showed absorptions at 3350 and 1030(OH), 1645 and 895(C=CH₂), and 1670 and 830(C=C) cm⁻¹. Its mass spectrum showed successive peaks of two series at m/e 408(M⁺-H₂O), 339, 271, 203, 135 and 357, 289, 221, 153, and base peak at 69 characteristic of those of polyprenoids^{1b,C)}. The PMR spectrum of II exhibited signals at δ 3.55(2H,d,J=6Hz,CH-CH₂OH), 1.60(15H,s) and 1.68(6H,s) due to allylic methyl, 2.00-2.07(19H,protons of allylic methylene and methine), 4.68 and 4.95(each 1H, broad s,C=CH₂), and 5.12(5H,broad,C=CH-). The CMR spectra of II showed the presence of a methine at 48.9(d), a methylene bearing oxygen at 64.1(t), and an olefinic methylene at

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111.1(t) ppm.

From these findings, it can be said that II is a polyprenol composed of six isoprene units and that the signal at $\delta 1.60$ are assignable to a methyl group of the ω -terminal and four methyl groups of the internal trans isoprene residue⁴⁾, and the signal at $\delta 1.68$ to a methyl group of the ω -terminal and a methyl group on the olefin in the α -terminal moiety.

The acetate(III, M⁺468.3984), obtained by acetylation of II with Ac_2O pyridine, was ozonized[-30°, 30 min in AcOEt/MeOH(4:1)] followed by oxidative workup(H_2O_2 -HCOOH) to yield levulinic acid(IV) and β -acetylbutyrolactone(V) [IR;1770, 1715cm⁻¹, PMR; δ 2.70(3H,s,COCH₃), 2.79(2H,d,J=8Hz,-CH₂CO-), 3.62(1H,q, J=7Hz,8Hz,-OCH₂CH \leq), 4.48(2H,d,J=7Hz,-OCH₂CH \leq)] and no succinic acid was characterized, revealing the non-squalene nature of the molecule.

As a result, it is clear that the α -terminal of II has an isopropenyl and a hydroxymethyl group on a methine⁵⁾, and all of the trans isoprene units linked in a "head-to-tail" manner.

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References and Footnotes

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