A New Chemical Constituent of Green Leaves of Ginkgo biloba L.

Bong Young Chung', Lee Sook Won, Boo Ryong Lee and Chai Ho Lee

Department of Chemistry, Korea University, Seoul 132, Korea
(Received June 9, 1981)

ABSTRACT. A new chemical constituent was isolated from the green leaves of Ginkgo biloba L. and identified as 3-(pentadec-8-enyl) phenol.

INTRODUCTION

The Ginkgo tree, Ginkgo biloba L., is the sole surviving species of the group of plants known as Ginkgoales and is thus called a fossil tree or living fossil. Because of this longevity and of its pharmacological usefulness, nearly all the parts of this tree, i.e., root, bark, heartwood, seeds, fruit, pollen and leaves have been subjected to numerous chemical investigations.

Of these, study of the leaves was commenced in 1929 by Furukawa, which led to the isolation of ginnol (10-nonacosanol) and the following chemical constituents have been afterwards identified: ginnon, 2-hexenal, shikimic acid, quinic acid, bilobalides, ginkgolides, β-sitosterol, cerryl alcohol, oxalic acid, linolenic acid, linoleic acid, palmitic acid, anacardic acid, carotenes, D-glucaric acid, vitamin C, hexosamines, and lignins.

The other important components of the leaves are bisflavanoids, i.e., ginkgetin, isoginkgetin and sciapopitysin. These phenolic compounds have vasodilating and spasmylytic activities and their aqueous solutions have recently been used for the treatment of peripheral arterial circulatory disturbances, intermittent claudication and vascular diseases of the limbs.

In connection with this pharmacological importance, we have reinvestigated the green leaves of Ginkgo tree and isolated a new, hitherto unreported chemical constituent: 3-(pentadec-8-enyl) phenol.

ISOLATION

The methanol extract of the air-dried and stem-free green leaves of male Ginkgo tree was filtered through celite and concentrated to a dark-red syrup, which was extracted with dichloromethane. Thin-layer chromatography of this solution on silica gel plate (Merck, F_{254}: CHCl_3-EtOAc 1:1) showed it was a mixture of at least 6 components, the r values of which...
were 0.92, 0.72, 0.54, 0.26, 0.15 and zero. From this mixture the component of rf value of 0.54 was separated as a pale yellow liquid (bp: 220~222°C) by successive silica gel column chromatography (1:1 6H-CHCl3).

**RESULTS AND DISCUSSION**

**IR Spectral Data.** The IR spectrum (neat) exhibited strong absorption bands at about 3380, 1585, 1450 cm−1 and relatively weak bands at 1910, 1830 and 1695 cm−1, in particular. The broad band centered at 3380 corresponds to the hydrogen–bonded OH stretching vibration. The absorption bands at 1585 and 1450 cm−1 indicate the presence of aromatic ring, and the aromatic overtone bands at 1910, 1830 and 1695 cm−1 further suggest that the ring is meta-disubstituted.

**Mass Spectral Data.** The mass spectrum revealed an apparent molecular ion peak at m/z=302 with fragment ions at 108 (base peak), 107, 69, 55, and 41. This corresponds to a probable C20H34O molecular composition, provided that there are no other elements present. The fragment ion peaks at 108 and 107 suggest it is a phenol or benzyl alcohol derivative, but the presence of base peak at 108 excludes the possibility of being a benzyl alcohol derivative. The characteristic fragmentation pattern of alkenes at 41, 55 and 69 also indicates that the meta-substituent is an olefinic group.

**UV Spectral Data.** The UV spectrum (in CHCl3) shows the phenolic secondary absorption band at 273 nm (ε=1, 440) with a shoulder at 279 nm (ε=1, 290).

**3H-NMR Spectral Data.** Assuming 3-alkenylnaphthalene as a plausible structure for this compound based on the above spectral data, the 3H-NMR spectrum (CDCl3, internal TMS) can be analyzed as follows: 4 aromatic protons (δ 7.20~6.45 ppm), 1 phenolic proton (6.65 ppm) which is D2O exchangeable, 2 vinylic protons (5.34 ppm), 2 methylene protons adjacent to the aromatic ring (2.64~2.32), 4 methylene protons adjacent to a double bond (2.32~1.80), 18 methylene protons (1.70~1.04) and 3 terminal protons (0.85 ppm).
methyl protons (0.85). Existence of only one methyl group, a double bond and 24 methylene protons indicate that the \textit{meta}-substituent of this phenol is a straight, pentadecenyl group, and the position of its double bond was ascertained by oxidative cleavage. In addition, the $^1$H-NMR spectrum of the acetylated compound revealed monoacetylation with the corresponding 3 protons at $\delta$ 2.23 ppm; which also confirms the presence of only one hydroxyl group in this phenolic compound.

**Position of Double Bond.** Oxidative cleavage of the acetylated product with KMnO$_4$-MgSO$_4$ in acetone\textsuperscript{38} and subsequent distillation yielded \textit{m}-heptanal (bp: 152$-$154$^\circ$C) as the lowest boiling fraction. This confirms that the double bond of the pentadecenyl side chain is located at the seventh carbon from terminal methyl group, and thus that the \textit{meta}-substituent of this phenol is pentadec-8-enyl group.

**CONCLUSION**

The spectral and chemical data of this constituent isolated from the green leaves of \textit{Ginkgo biloba L.} establish its structure as 3-(pentadec-8-enyl) phenol, although the stereochemistry of the double bond could not be clearly verified. 3-(Pentadec-8-enyl) phenol (C$_{21}$H$_{34}$O, bp: 220$-$222$^\circ$C) happens to be identical with ginkgol (C$_{21}$H$_{34}$O, bp: 221$-$225$^\circ$C)\textsuperscript{32}, a known constituent of the seeds\textsuperscript{32,34} and of the fruit\textsuperscript{33,34} of Ginkgo tree. But ginkgol has never been claimed to be a chemical constituent of the Ginkgo leaves.

**REFERENCES**

25. The financial support of this work by the Ministry of Education is gratefully acknowledged.