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ISOLATION AND STRUCTURE OF GYMNOPRENOL-D, A HOMOLOGOUS SERIES OF FULLY HYDRATED POLYISOPRENEPOLYOL FROM GYMNOPILUS SPECTABILIS

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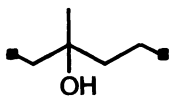
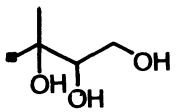
Gymnoprenol-D, a homologous series of fully hydrated polyisoprenepolyol having a glycerol terminus has been isolated from an hallucinogenic mushroom, Gymnopilus spectabilis along with an analogous compound with one double bond. The structure of these polyols was determined by a combination of chemical degradation and spectroscopic analyses.

Recently we reported the isolation and structures of gymnoprenol-A, -B and a bitter principle gymnopilin, all of which belong to a novel type of polyisoprene chain from the fruiting bodies of Gymnopilus spectabilis.[1-3] These polyols occur as a mixture of the isoprene homologs composed of 45 to 60 carbon atoms. Druing the course of the study on the constituents of this mushroom, it was observed that there is more hydrophilic polyisoprenepolyol in the aqueous layer when the extracts of the mushroom were partitioned between water and ethyl acetate. In the present communication we describe the isolation and structural determination of the homologous series of this polyisoprenepolyol, gymnoprenol-D (G-D), containing 12 to 14 hydroxy groups in the polyisoprene chain consisting of 10 to 12 isoprene units. An analogous polyol, gymnoprenol-E (G-E), containing one double bond was also isolated as a mixture of homologs.

The dried fruiting bodies (388 g) of the mushroom were extracted with methanol. The extracts were concentrated and partitioned between water and ethyl acetate. The diluted aqueous layer was then slowly passed through a column of Amberlite XAD-2. The adsorbed materials were eluted with methanol, and the eluate was chromatographed on a Florisil column (prewashed with methanol) to yield crude gymnoprenols (2.6 g). The fractions containing mainly G-D and G-E (G-D : G-E = Ca. 3 : 2) were further purified by preparative HPLC (SH-343,ODS/MeOH-water) to give pure specimens as a mixture of isoprene homologs.

Gymnoprenol-D (Rt on HPLC, 4.7 min) showed three molecular ion peaks in the SIMS at m/z 917(M^++Na), 1003(M^++Na), and 1089(M^++Na), which indicated that G-D is a mixture of three isoprene homologs with the molecular formulae of $C_{50}H_{102}O_{12}$, $C_{55}H_{112}O_{13}$, and $C_{60}H_{122}O_{14}$. That the molecular formulae contain no unsaturation was supported by its ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum (CD_3OD) of G-D (1) showed intense signals at 1.14(s) and 1.40(m) in a ratio of 1 : 2 . These signals were assigned to the protons of a tertiary methyl on a carbon bearing a hydroxy group and three methylenes, respectively, revealing the presence of the repeated structural units such as (i). The prominent ^{13}C NMR (CD_3OD) signals at


(i)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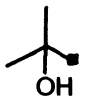
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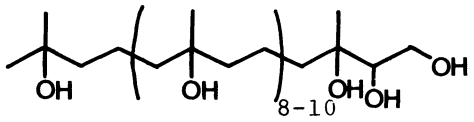
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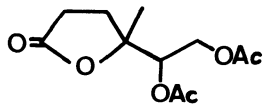
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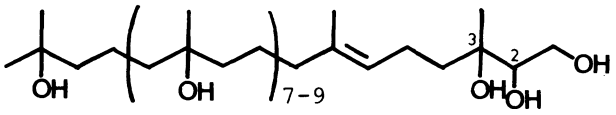
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26.8(q), 73.0(s), 19.0(t), and 43.0(tt) could be assigned to the carbons in the unit (i). The presence of the triol moiety (ii) was supported by the ^{13}C NMR signals at 22.4(q), 63.6(t), 77.5(d), and 74.6(s) and the ^{1}H NMR signals from 3.5 to 3.8(3H), the latter shifting to 4.06(dd, J=9.0, 12.0 Hz), 4.53(dd, J=2.5, 12.0 Hz), and 5.06(dd, J=2.5, 9.0 Hz) in the diacetate 2. The remaining signals at 29.1(q), 29.6(q), and 71.0(s) in the ^{13}C NMR spectrum of 1 were assigned to the carbons in the terminal unit (iii). From the spectral properties (SIMS, ^{1}H and ^{13}C NMR) mentioned above, it was concluded that G-D possesses eight to ten repeated structural units (i) along with a (ii) and a (iii), and its structure should be represented by 1.

A minor constituent, gymnoprenol-E (Rt on HPLC, 6.3 min), exhibited molecular ion peaks in the FAB mass spectrum at m/z 899(M^++Na), 985(M^++Na), and 1071(M^++Na), which correspond to the molecular formulae of $C_{50}H_{100}O_{11}$, $C_{55}H_{110}O_{12}$, and $C_{60}H_{121}O_{13}$, respectively. The ^{1}H NMR and ^{13}C NMR spectra of G-E (3) are almost the same as those of 1 excepting the ^{13}C NMR signals at 135.4(s) and 124.6(d) and the ^{1}H NMR signal at 5.11(m, 1H), which indicate the presence of a trisubstituted double bond in 3.[5] The position of the double bond in 3 was determined on the basis of the formation of the lactone 5 on ozonolysis of the corresponding diacetate 4.[1]

Further studies on the stereochemistry of the chiral centers are under way.[6]

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References

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3)F.Aoyagi, S.Maeno, T.Okuno, H.Matsumoto, M.Ikura, K.Hikichi, and T.Matsumoto, Tetrahedron Lett., 24, 1991 (1983).
4)HPLC conditions; column:A-312(ODS), 6 mm x 150 mm, MeOH-water=80:20v/v%, flow rate: 1.0 ml/min, pressure:60 kg/cm^2.
5)A signals at 15.9(q) in 3 indicates trans geometry of the double bond;see Ref. 1.
6)Stereochemistries at C-2 and C-3 in the related compounds G-A and gymnopilin have been determined as S and R, respectively : S.Nozoe, Y.Koike, and G.Kusano, Tetrahedron Lett., in press.

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