Chem. Pharm. Bull. 20(3) 514—520 (1972)

UDC 547.917.02 : 581.193

Studies on Resin Glycosides. III.[1] Complete Structures of Pharbitic Acids C and D

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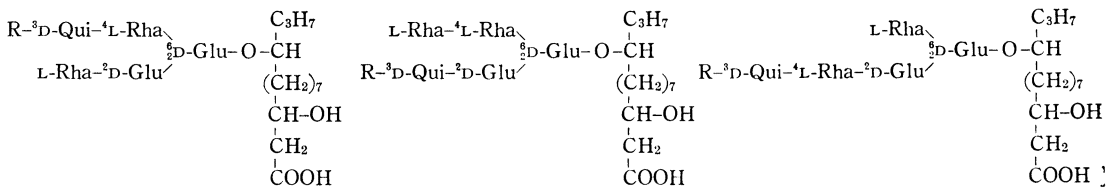
(Received July 31, 1971)

Pharbitic acids C (II) and D (III), the two major constituents of "pharbitic acid" (I), were shown to have the monosaccharide sequences IIa and IIIa among the three IIa—c and IIIa—c, respectively, by characterization of their acetolysis products and examination of mass spectra of their permethylates (XI and XII).

The modes of linkages and conformations of the component monosaccharides were determined by molecular rotation differences and NMR spectra of II, III, and degradation products (IV, V, XIII, XIV and XV) and their permethylates (VI, VII, VIII, IX, XVI, XVII, XI and XII) to be α-conjugation and 1C conformation for L-rhamnose and β and Cl for D-glucose and D-quinovose.

Consequently II and III are assigned the structures IIa' and IIIa', respectively.

In the preceding paper[1b] of this series, it was reported that "pharbitic acid" (I) is a mixture of at least four compounds and the major two constituents, pharbitic acids C (II) and D (III), are respectively considered to be one of the following three branched-chain penta- (IIa—c) and hexaglycosides (IIIa—c) of ipurolic (3,11-dihydroxytetradecanoic) acid.



IIa: R=H
IIIa: R=L-Rha

IIb: R=H
IIIb: R=L-Rha

IIc: R=H
IIIc: R=L-Rha

Chart 1

This paper deals with the determination of sequences, modes of linkages and conformations of the componont monosaccharides in II and III.

When I was heated with acetic anhydride in the presence of anhydrous zinc chloride, the product showed on thin-layer chromatography (TLC) five spots, (a), (b), (c), (d) and (e) in the order of increasing polarity (Fig. 1), among which the spot (b) turned black and other four showed yellow to brownish yellow on heating with 10% sulfuric acid. Taking *Rf* values and colors into account, it was presumed that the spot (a) is that of methylpentose acetate, (b) glucose acetate, (c) and (d) methylpentobiose acetates and (e) methylpentotriose acetate. The acetolysis product of I was chromatographed on silica gel column using benzene–acetic acid giving four fractions (Fr. 1—4). Fr. 1 was a mixture of peracetates of methylpentose and glucose (spots (a) and (b)), and Fr. 2, 3 and 4 showed on TLC the single spot of (c), (d) and (e), respectively.

1) *a*) Preliminary communication: H. Okabe and T. Kawasaki, *Tetrahedron Letters*, **1970**, 3123; *b*) Part II: H. Okabe, N. Koshito, K. Tanaka and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **19**, 2394 (1971).

2) Location: *Katakasu, Fukuoka.*

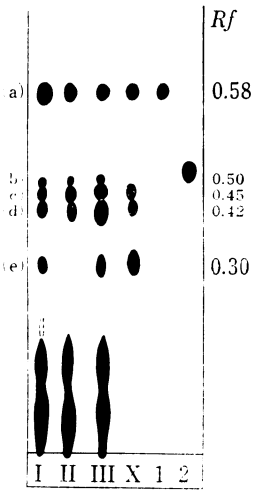


Fig. 1. TLC[a] of Acetolysates of I, II, III and X

1. 1,2,3,4-tetra-O-acetyl-α-L-rhamnopyranose (reference)
2. 1,2,3,4,6-penta-O-acetyl-α-D-glucopyranose (reference)
a) Kieselgel G nach Stahl, 3% EtOH in benzene

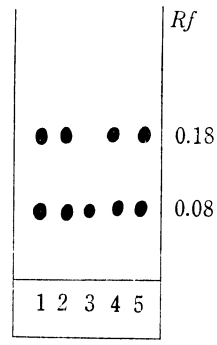


Fig. 2. TLC[a] of Deacetylation Products

1: Fr. 2 of acetolysate of I,
2: Fr. 3 of acetolysate of I,
3: methylpentobiose acetates obtained from II,
4: methyl pentobiose acetates from III,
5: methylpentobiose acetates obtained from X.
a) Kieselgel G nach Stahl, $CHCl_3$–MeOH–H_2O (7:3:1, bottom layer)

When Fr.2 and Fr.3 were respectively treated with a catalytic amount of sodium methoxide in methanol,[3] both gave the same mixture of two reducing sugars (Fig. 2) suggesting that Fr. 2 contained two kinds of methylpentobiose peracetate and Fr. 3 consisted of two corresponding anomers. The two reducing sugars were separated in TLC homogeneous state by chromatography on silica gel using $CHCl_3$–MeOH–H_2O (7:3:1, bottom layer). The less polar one (IV) showed the infrared (IR) absorption of acetoxyl group at 1740 cm^{-1} and analyzed for $C_{14}H_{24}O_{10}$ indicating it to be a methylpentobiose monoacetate and the more polar one (V)[4] showed no IR absorption of acetoxyl group and analyzed for $C_{12}H_{22}O_9 \cdot 1/2\ H_2O$.

When IV and V were respectively acid hydrolyzed[5] and examined by paper chromatography (PC) according to the Krauss method,[6] L-rhamnose and D-quinovose were detected in both cases. IV was methylated[5] according to the Haworth method[7] followed by the Hakomori's[8] to give a pair of permethylates; VI, $[\alpha]_D$ −46.1°, $C_{18}H_{34}O_9$, *Rf* (hexane:AcOEt= 2:1, Kieselgel G), 0.32 and VII, $[\alpha]_D$ +11.3°, $C_{18}H_{34}O_9$, *Rf*; 0.17. They were methanolyzed to yield methyl 2,3,4-tri-O-methyl-α-L-rhamnopyranoside and methyl di-O-methyl-α- and -β-D-quinovosides. Since the latter two are to be originated from III in I and the D-quinovose unit in III is combined with L-rhamnose at the C_3-hydroxyl group,[1b] VI and VII are anomeric methyl L-rhamnopyranosyl-(1–3)-D-quinovopyranoside permethylates and IV is regarded as L-rhamnopyranosyl-(1–3)-D-quinovose monoacetate.

3) A. Thompson, M.C. Wolfrom and E. Pascu, "Methods in Carbohydrate Chemistry," Vol. II, ed. by R. L. Whistler and M.L. Wolfrom, Academic Press Inc., New York and London, 1963, p. 216.
4) When Fr. 2 was treated with a small amount of methanol, a white powder was precipitated which was recrystallized from the same solvent to give a colorless compound; mp 160—161°, $[\alpha]_D^{12}$ −59.7°, $C_{24}H_{34}O_{15} \cdot 1/2\ H_2O$. NMR (ppm): 1.25 (3H, d, J=6.0 Hz, -CH-C$\underline{H}_3$), 1.35 (3H, d, J=6.0 Hz, -C$\underline{H}$-C$\underline{H}_3$), 2.0—2.2 (18H, -OCOC$\underline{H}_3$×6), 6.0 (1H, s, H next to the anomeric acetoxyl group). This compound furnished only V when treated with sodium methoxide.
5) An acetoxyl group in IV was removed.
6) M.T. Krauss, H. Jäger, O. Schindler and T. Reichstein, *J. Chromatog.*, 3, 63 (1960).
7) E.L. Hirst and E. Percival, "Methods in Carbohydrate Chemistry," Vol. II, p. 146.
8) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 255 (1964).

V was methylated in the same manner to yield two permethylates, VIII, $[\alpha]_D$ −64.6°, $C_{18}H_{34}O_9$, *Rf* (hexane:AcOEt=2:1, Kieselgel G); 0.36, and IX, $[\alpha]_D$ +3.7°, $C_{18}H_{34}O_9$, *Rf*: 0.22, both of which gave, on methanolysis, methyl 2,3,4-tri-O-methyl-α- and -β-D-quinovopyranosides and methyl 2,3-di-O-methyl-α-L-rhamnopyranoside. Accordingly VIII and IX are thought to be anomeric methyl D-quinovopyranosyl-(1–4)-L-rhamnopyranoside permethylates and V is regarded as D-quinovopyranosyl-(1–4)-L-rhamnose.

Fr. 4 was crystallized from methanol giving a white powder (X), mp 193—195°, $[\alpha]_D$ −50.7°, $C_{34}H_{48}O_{21}\cdot H_2O$. Its nuclear magnetic resonance (NMR) spectrum showed three doublets at 1.15 ppm (3H, J=5.3 Hz), 1.25 ppm (3H, J=5.3Hz) and 1.33 ppm(3H, J=6.0 Hz), the signals (24 H in total) due to eight acetoxyl groups at 1.9—2.3 ppm and a singlet (1H) at 5.98 ppm attributable to the proton next to an anomeric acetoxyl group. The molecular formula and NMR data indicate X to be the peracetate of a methylpentotriose. X gave, on further acetolysis, methylpentobiose acetates (Fig. 1) which were treated with sodium methoxide to give IV and V (Fig. 2) indicating that the monosaccharide sequence in X is L-rhamnopyranosyl-(1–3)-D-quinovopyranosyl-(1–4)-L-rhamnose.

Acetolysis of III in the same condition gave the same product as that from I, while II treated likewise did not provide X, and two methylpentobiose acetates (Fig. 1) were afforded, which were deacetylated to give only V (Fig. 2).

These results indicate that there exist in II and III the D-quinovopyranosyl-(1–4)-L-rhamnose and the L-rhamnopyranosyl-(1-3)-D-quinovopyranosyl-(1-4)-L-rhamnose units, respectively, and hence among three possible sequences (IIa—c and IIIa—c), IIb and IIIb are excluded.

Since chemical assignment of the sequences of II and III to either one of the remanining two seemed hardly accessible, the mass spectral analyses of permethylates (XI and XII) of II and III were then carried out. Their spectra (*m/e* 200—400 region) and the most probable structures of the characteristic fragment ions are shown in Fig. 3.

XI gave, besides the fragment peaks at *m/e* 239 (A) and 271 (B) originated from the aglycone, those at *m/e* 331, 361, 363 and 393. In consideration of the two possible sequences

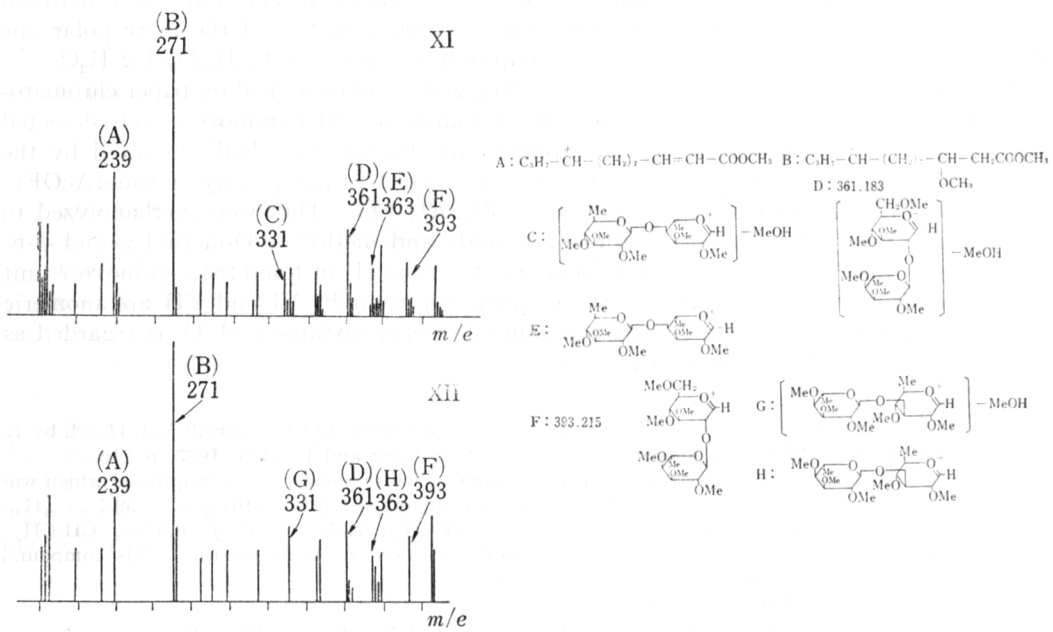


Fig. 3. Mass Spectra[a] of XI and XII

a) All peak heights are relative to that of *m/e* 271.

IIa and IIc and of the observation of Kováčik, *et al.*[9] that the cracking of the fully methylated oligosaccharide follows the similar pattern as that of methylated monosaccharide, the structures of *m/e* 363 and 331 ions were presumed as (E) and (C), respectively, and accurate mass determination of *m/e* 393 and 361 ions indicated that the former is (F) or its isomer and the latter is (D) or its isomer. The formation of the *m/e* 393 and 361 ions can be explained only by the sequences IIa where the rhamnopyranosylglucopyranose unit is located at a terminal. The mass spectrum of XII also exhibited the peaks at *m/e* 331, 361, 363 and 393 and these fragment ions are assigned the structutes (G), (D), (H) and (F), respectively.

Consequently II and III are represented by the formulas IIa and IIIa respectively, where all monosaccharides are in pyranose form.

In order to determine the modes of linkages and conformations of the component monosaccharides of II and III, the molecular rotations and NMR spectra were taken. The mole-

Table I. Molecular Rotation Differences

	$[\alpha]_D$ (MeOH)	$[M]_D$	$\Delta[M]_D$
Methyl ipurolate	+ 1.33°	+ 3.64°	
XIII	−16.2°	−70.5°	−74°
XIV	−23.6°	−143.0°	−72°
XV	−25.9°	−192.5°	−52°
Methyl pyranosides of			
α-D-glucose		+307°[10]	
β-D-glucose		− 62°[10]	
α-L-rhamnose		−109°[11]	
β-L-rhamnose		+169°[11]	

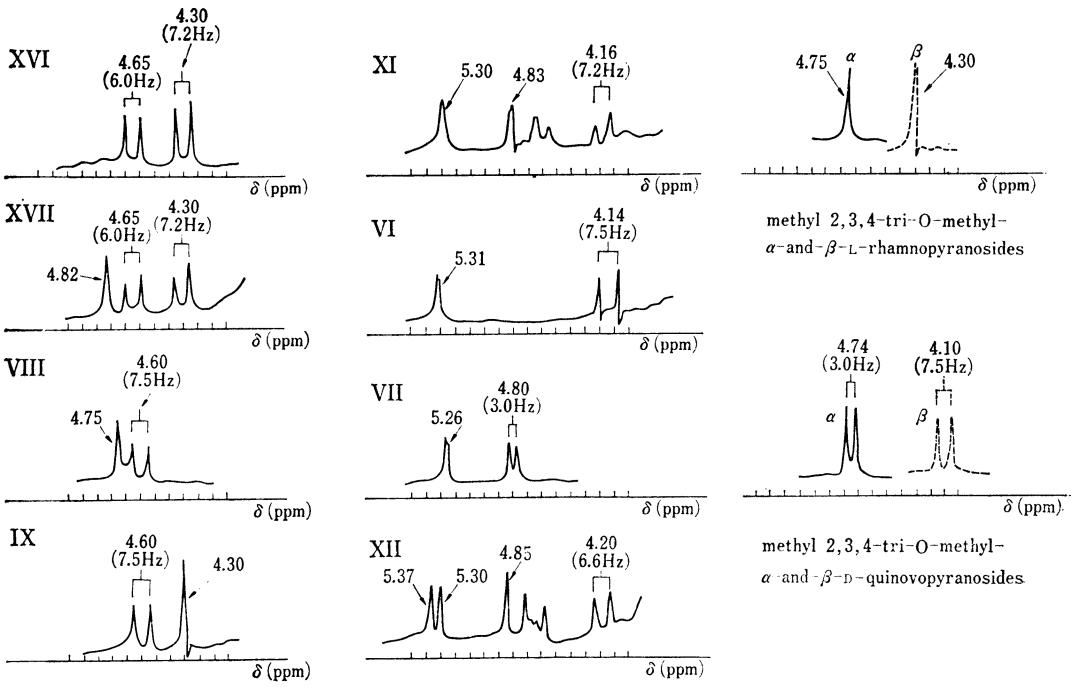


Fig. 4. NMR Spectra of Anomeric Protons (60 MHz, $CDCl_3$)

9) V. Kováčik, Š. Bauer and J. Rosík, *Carbohyd. Res.*, **8**, 291 (1968).
10) E. Pascu, "Methods in Carbohydrate Chemistry," Vol. II, p. 356.
11) E. Fischer, M. Bergmann and A. Rabe, *Chem. Ber.*, **53**, 2364 (1920).

cular rotation differences (Table I) of methyl ipurolate, its mono-D-glucopyranoside (XIII),[1b] D-glucopyranosyl-(1-2)-D-glucopyranoside (XIV)[1b] and D-glucopyranosyl-(1-2)-[L-rhamnopyranosyl-(1-4)-]-D-glucopyranoside (XV)[1b] indicated that the glycosidic linkages are presumed to be α for L-rhamnose and β for D-glucose units.

Permethylate (XVI) of XIV exhibited on NMR spectrum (Fig. 4) two doublets (4.30 pm, J=7.2 Hz; 4.65 ppm, J=6.0 Hz) due to two anomeric protons of β-D-glucopyranosyl groups in Cl conformation,[12] and permethylate (XVII) of XV exhibited, besides the above two doublets, a singlet at 4.82 ppm attributable to the anomeric proton of L-rhamnopyranosyl residue (Fig. 4). When the α-L-rhamnopyranose residue has the Cl conformation, the anomeric proton (axial) should appear as a doublet with a coupling constant of 6—8 Hz, while in 1C conformation it (equatorial) is expected to be a singlet or a doublet with much smaller coupling constant (<3 Hz).[12] From the NMR signal (singlet) of the anomeric proton of the L-rhamnose unit in XVII, it is regarded to have the 1C conformation.

One (VIII) of the permethylates obtained from V showed the anomeric proton signals as a doublet at 4.60 ppm (J=7.5 Hz) and a singlet at 4.75 ppm, and its anomer (IX) exhibited a doublet at 4.60 ppm (J=7.5 Hz) and a singlet at 4.30 ppm (Fig. 4). In consideration of the anomeric proton signals (singlets at 4.75 and 4.30 ppm) of methyl 2,3,4-tri-O-methyl-α- and -β-L-rhamnopyranosides (Fig. 4), the singlets at 4.75 ppm (of VIII) and at 4.30 ppm (of IX) are assigned respectively to α- and β-L-rhamnopyranose residue and the doublet at 4.60 ppm should be due to the D-quinovose unit and the coupling constant indicates that it is β-linked in Cl conformation.[12]

NMR spectrum of XI shows two singlets at 4.83 and 5.30 ppm (Fig. 4). In comparison with that of XVII, the former singlet is attributable to the anomeric proton of α-L-rhamnopyranose residue combined with C_6-hydroxyl group of glucose and hence the latter is thought to be due to that of the terminal L-rhamnopyranosyl group linked to C_2-hydroxyl group of glucose and the mode of linkage is assumed to be α as generally is the case with natural L-rhamnopyranosides. This assignment is supported by the Röslers observation[13] that the anomeric proton of the α-L-rhamnose of trimethylsilylated neohesperidoside (2-O-α-L-rhamnopyranosyl-β-D-glucopyranoside) of flavonoids appears in the lower magnetic field (4.9—5.0 ppm) than that (4.2—4.4 ppm) of trimethylsilylated rutinoside (6-O-α-L-rhamnopyranosyl-β-D-glucopyranoside). The terminal rhamnose unit which is α-conjugated is to have the 1C conformation because its anomeric proton appeared as a singlet.

On the basis of all the results described above the complete structure of II is proposed as IIa'.

One (VI) of the permethylates prepared from IV which is originated from III exhibited on NMR spectrum (Fig. 4), a doublet at 4.14 ppm (J=7.5 Hz) and a singlet at 5.31 ppm attributable to two anomeric protons, and its anomer(VII) showed a doublet at 4.80 ppm (J= 3.0 Hz) and a singlet at 5.26 ppm. Because the anomeric protons of synthesized methyl 2,3,4-tri-O-methyl-α- and -β-D-quinovopyranosides[1b] showed doublets at 4.74 ppm (J=3.0 Hz) and 4.10 ppm (J=7.5 Hz), respectively, the singlets at 5.31 and 5.26 ppm in VI and VII are attributed to the anomeric proton of L-rhamnose residue and hence VI and VII are regarded as methyl L-rhamnopyranosyl-β- and -α-D-quinovopyranoside permethylates, respectively. The molecular rotation difference (−98.8°) between VI ($[M]_D$ −181.7°) and methyl 2,3,4-tri-O-methyl-β-D-quinovopyranoside ($[M]_D$ −82.9°) is in good agreement with that ($[M]_D$ −98.3°) of methyl 2,3,4-tri-O-methyl-α-L-rhamnopyranoside suggesting the α-conjugation of L-rhamnopyranosyl group to D-quinovose in VI, and the above mentioned NMR signal (singlet) of the anomeric proton indicates that L-rhamnose is in 1C conformation.

12) L.D. Hall, *Advan. Carbohydrate Chem.*, **19**, 51 (1964); K. Miyahara and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1369 (1969).
13) H. Rösler, T.J. Mabry, M.F. Cranmer and J. Kagan, *J. Org. Chem.*, **30**, 4346 (1965).

Consequently the full structure of III is represented by the formula IIIa' and the conclusion is supported by the NMR spectrum of XII (Fig. 4) in comparison with that of XI.

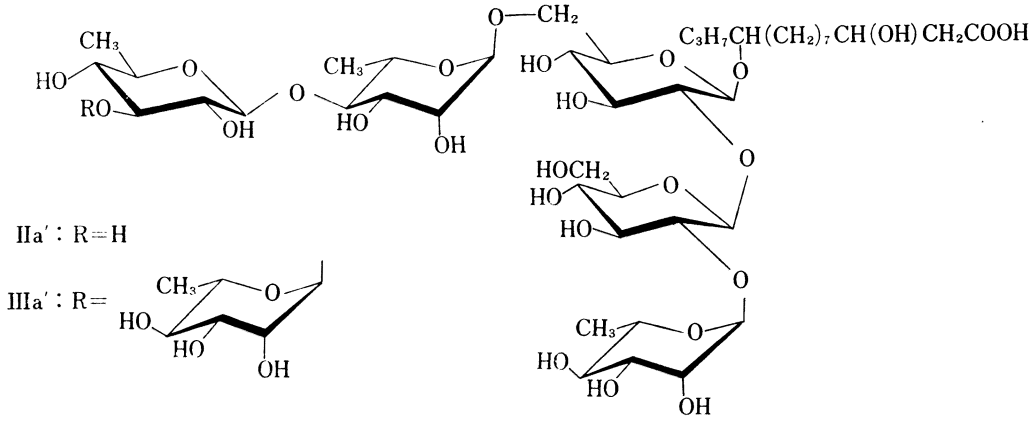


Chart 2

Experimental[14]

Acetolysis of "Pharbitic Acid" (I)——I (20 g) and freshly fused $ZnCl_2$ (20 g) were dissolved in Ac_2O (150 ml) and heated at 90° for 1 hr. The reaction mixture was poured into ice water, neutralized with $NaHCO_3$, and extracted with ether (1 liter in total). The ether layer was washed with H_2O, dried over Na_2SO_4 and evaporated to yield a black resin (32.5 g) (TLC, Fig. 1). The resin (10 g) was chromatographed on silica gel (100 g) giving four fractions. Fr. 1 (eluant, 3% AcOH in benzene; yield, 2.1 g) showed two spots (*Rf* 0.58 and 0.50) on TLC (Kieselgel G, 3% EtOH in benzene) (1,2,3,4-tetra-O-acetyl-α-L-rhamnopyranose, *Rf* 0.58; 1,2,3,4,6-penta-O-acetyl-α-D-glucopyranose, 0.50). Fr. 2 (5% AcOH: 0.6 g; TLC, *Rf* 0.45)[4] and Fr. 3 (5% AcOH; 0.3 g; TLC, *Rf* 0.42) were respectively puffed *in vacuo* to give a white powder. Fr. 4 (10% AcOH; 0.6 g; TLC, *Rf* 0.30) was crystallized from MeOH to give colorless needles (X), mp 193—195°, $[\alpha]_D^{18}$ −50.7° (*c*=1.05, $CHCl_3$). *Anal.* Calcd. for $C_{34}H_{48}O_{21}\cdot H_2O$: C, 50.37; H, 6.17. Found: C, 50.59; H, 6.15. NMR (ppm): 1.15 (3H, d, *J*=5.3 Hz, -ĊH-CH$_3$), 1.25 (3H, d, *J*=5.3 Hz, -ĊH-CH$_3$), 1.33 (3H, d, *J*=6.0 Hz, -ĊH-CH$_3$), 1.9—2.2 (24H in total, -OCOCH$_3$×8), 5.98 (1H, s, H next to the anomeric acetoxyl group).

Treatment of Fr. 2 and Fr. 3 with MeONa——Fr. 2 (22 mg) and Fr. 3 (25 mg) were respectively dissolved in absolute MeOH (1 ml), 0.5% MeONa in MeOH (0.07 ml) was added and stirred at room temperature for 90 min. To the reaction mixture, H_2O (2 ml) and ion exchange resin Amberlite IR-120 (H^+) (200 mg) were added and stirred for a few minutes. The filtrate was evaporated *in vacuo* and the residue was examined by TLC. The results are shown in Fig. 2.

Isolation of Methylpentobioses (IV) and (V)——The deacetylation product (850 mg) of Fr. 2 and Fr. 3 was chromatographed on silica gel (40 g) using $CHCl_3$–MeOH–H_2O (7:3:1, bottom layer) to give IV (230 mg) and V (200 mg). IV: an amorphous powder, $[\alpha]_D^{16}$ −2.3° (*c*=1.1, MeOH). *Anal.* Calcd. for $C_{14}H_{24}O_{10}$: C, 47.72; H, 6.81. Found: C, 47.72; H, 6.99. IR ν_{max}^{KBr} cm^{-1}: 1740 (-OCOCH$_3$). NMR (pyridine, ppm): 2.30 (3H, s, -OCOCH$_3$). V: an amorphous powder, $[\alpha]_D^{16}$ −11.6° (*c*=1.13, MeOH). *Anal.* Calcd. for $C_{12}H_{22}O_9\cdot\frac{1}{2}H_2O$; C, 45.14; H, 7.21. Found: C, 45.37; H, 7.22.

Identification of Component Monosaccharides of IV and V——IV and V (10 mg each) were respectively acid hydrolyzed with 2N HCl (0.5 ml) at 90° for 1 hr, worked up as usual, and the product was examined by PC according to the Krauss method.[6] In each case, two spots (*R*Rha[15] 0.66, 1.00) (D-quinovose 0.66) were detected.

14) All melting points were taken on a Kofler block and are uncorrected. NMR spectra were determined on a JEOL-JNM-C-60H spectrometer in deuteriochloroform solution unless otherwise specified and chemical shifts are given in δ-scale with tetramethylsilane as internal reference (s, singlet; d, doublet). Mass spectra were taken on a JEOL-JNM-OISG spectrometer provided with a glass inlet system heated at 150°, ion accelerating voltage, ionizing voltage, ionizing current being 4.6 KV, 30 eV and 200 A, respectively. TLC was conducted on Kieselgel G nach Stahl. In column chromatography "Kanto" silica gel (100—200 mesh) was employed. In PC and GLC, Toyo Roshi No. 2 and Shimazu GC-3AF Gas Chromatograph were used, respectively.

15) Movement relative to that (*ca.* 15 cm) of L-rhamnose.

Permethylates (VI and VII) of IV——IV (65 mg) was dissolved in H_2O (0.3 ml), Me_2SO_4 (0.5 ml) and 30% NaOH (0.5 ml) were added and stirred for 24 hr. Me_2SO_4 (0.2 ml) and 30% NaOH (0.4 ml) were further added and stirred until the reaction mixture did not reduce the Fehling solution (*ca.* 3 hr). The mixture was neutralized with 10% H_2SO_4 and extracted with CH_2Cl_2 (30 ml in total). CH_2Cl_2 layer was washed with H_2O, dried over Na_2SO_4 and evaporated to give an oil, which was permethylated according to the Hakomori method.[8] The product was chromatographed on silica gel (3 g) using hexane–AcOEt (2:1) as eluant to give VI (15.7 mg) and VII (5 mg) as syrups. VI: $[\alpha]_D^{21}-46.1°$ ($c=0.78$, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{34}O_9$: C, 54.82; H, 8.63. Found: C, 55.19; H, 8.83. NMR (ppm): 1.25 (3H, d, $J=6.0$ Hz, -ĊH-C$\underline{H}_3$), 1.30 (3H, d, $J=6.0$ Hz, -ĊH-C$\underline{H}_3$), 3.4—3.6 (18H in total, -OC$\underline{H}_3\times 6$), 4.14 (1H, d, $J=7.5$ Hz, anomeric H) and 5.31 (1H, s, anomeric H). VII: $[\alpha]_D^{25}+11.3°$ ($c=2.30$, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{34}O_9$: C, 54.82; H, 8.63. Found: C, 55.41; H, 8.82. NMR (ppm): 1.30 (6H, d, $J=7.5$ Hz, -ĊH-C$\underline{H}_3\times 2$), 3.4—3.6 (18H in total, -OC$\underline{H}_3\times 6$), 4.80 (1H, d, $J=3.0$ Hz, anomeric H) and 5.30 (1H, s, anomeric H).

Permethylates (VIII and IX) of V——V (100 mg) was methylated and worked up in the same manner as described above to give VIII (19 mg) and IX (17 mg) as colorless syrups. VIII: $[\alpha]_D^{17}-64.6°$ ($c=0.93$, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{34}O_9$: C, 54.82; H, 8.63. Found: C, 54.58; H, 8.73. NMR (ppm): 1.22 (3H, d, $J=6.0$ Hz, -ĊH-C$\underline{H}_3$), 1.31 (3H, d, $J=4.5$ Hz, -ĊH-C$\underline{H}_3$), 3.3—3.7 (18H in total, -OC$\underline{H}_3\times 6$), 4.60 (1H, d, $J=7.5$ Hz, anomeric H), and 4.75 (1H, s, anomeric H). IX: $[\alpha]_D^{17}+3.7°$ ($c=0.85$, $CHCl_3$). *Anal.* Calcd. for $C_{18}H_{34}O_9$: C, 54.82; H, 8.63. Found: C, 54.66; H, 8.78. NMR (ppm): 1.23 (3H, d, $J=6.0$ Hz, -ĊH-C$\underline{H}_3$), 1.35 (3H, d, $J=6.0$ Hz, -ĊH-C$\underline{H}_3$), 3.5—3.7 (18H in total, -OC$\underline{H}_3\times 6$), 4.30 (1H, s, anomeric H) and 4.60 (1H, d, $J=7.5$ Hz, anomeric H).

Identification of Component Monosaccharides of VI, VII, VIII and IX——VI, VII, VIII and IX (*ca.* 5 mg each) were respectively dissolved in 1N-HCl in MeOH (0.5 ml) and refluxed for 1 hr. MeOH (5 ml) was added and neutralized with Ag_2O. Precipitates were filtered off and the filtrate was evaporated *in vacuo*. The residue was examined by gas liquid chromatography (GLC). The results are shown in Table II.

Table II. Retention Times in GLC of Component Sugars of VI, VII, VIII and IX

Condition	t_R (min) I[a]	t_R (min) II[b]
VI	1.8, 2.6, 3.6, 5.0	7.1, 9.1
VII	1.8, 2.6, 3.6, 4.9	7.1, 9.1
VIII	1.4, 1.8, 4.9	5.2, 6.7
IX	1.4, 1.8, 4.9	5.2, 6.6
Methyl pyranoside of		
2,3,4-tri-O-methyl-α-L-rhamnose	1.8	7.1
-β-	2.6	9.1
2,3,4-tri-O-methyl-α-D-quinovose	1.8	6.6
-β-	1.4	5.2
2,3-di-O-methyl-α-L-rhamnose	4.9	

a) 5% 1,4-butanediol succinate on Shimalite W (60—80 mesh), 1.8 m × 4 mmϕ; temperature, 150°; carrier, N_2, 60 ml/min
b) 3% OV-17 on Chromosorb W (AW) DMCS (80—100 mesh), 1.7 m × 4 mmϕ; temperature, 138.5°; carrier, N_2, 18 ml/min

Acetolysis of II, III and X——II and III (60 mg each) were respectively acetolyzed as in I. III gave the same product (Fig. 1 and Fig. 2) as that from I, while the product (70 mg) from II in which no X was detected (Fig. 1) was column chromatographed on silica gel (2 g) using 3% AcOH in benzene as an eluant to give a fraction of methylpentobiose acetate (oil) which was deacetylated with MeONa to afford only V (Fig. 2). The same treatment of X gave the results shown in Fig. 1 and Fig. 2.

Mass Analyses of XI and XII (Fig. 3)——XI: *m/e* 393 (F) (Found: 393.215; Calcd. for $C_{18}H_{33}O_9$: 393.213), 363 (E) (Found: 363.203; Calcd. for $C_{17}H_{31}O_8$: 363.202), 361 (D) (Found: 361.183; Calcd. for $C_{17}H_{29}O_8$: 361.186), 331 (C), 271 (B), 239 (A). XII: *m/e* 393 (F), 363 (H), 361 (D), 331 (G), 271 (B) and 239 (A).