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Studies on the Constituents of *Momordica charantia* L. I. Isolation and Characterization of Momordicosides A and B, Glycosides of a Pentahydroxy-cucurbitane Triterpene[1]

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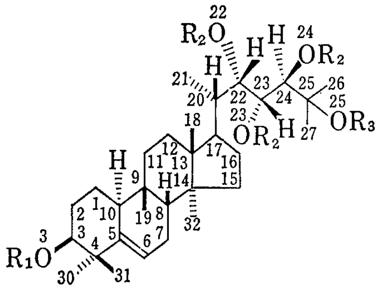
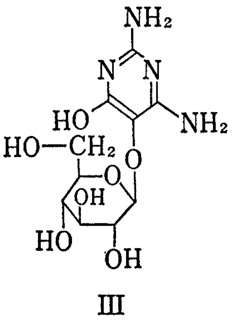
Two triterpene glycosides, momordicosides A and B, were isolated from the seeds of *Momordica charantia* L. (Cucurbitaceae). Their structures were determined on the basis of spectral and chemical evidence and by X-ray analysis as the 3-O-β-gentiobioside and 3-O-β-D-xylopyranosyl(1→4)-[β-D-glucopyranosyl(1→6)]-β-D-glucopyranoside, respectively, of cucurbit-5-ene-3β,22(*S*),23(*R*),24(*R*),25-pentaol.

Keywords——*Momordica charantia* L.; Cucurbitaceae; momordicosides A and B; vicine; cucurbit-5-ene-3β,22(*S*),23(*R*),24(*R*),25-pentaol; 9-methyl-19-norlanost-5-ene-3β,22(*S*),23(*R*),24(*R*),25-pentaol; X-ray crystallographic analysis; cucurbitane; triterpene glycoside

The fruit of *Momordica charantia* L. (Cucurbitaceae) (Niga-uri or Tsuru-reishi in Japanese) has been used as a bitter stomachic in southern Japan, and as a laxative and an anthelmintic for children in India.[3] An antidiabetic effect of its alcohol extract was also reported.[4]





III

I: R_1=D-Glu.pyr.^{1}——^{6}D-Glu.pyr.^{1}——
β β
$R_2=R_3=H$

II: R_1=D-Glu.pyr.^{1}╲$_6$
β D-Glu.pyr.^{1}——
D-Xyl.pyr.$_1$╱^{4} β
β
$R_2=R_3=H$

IV: $R_1=R_2=R_3=H$

V: $R_1=R_2=Ac$, $R_3=H$

VI: $R_1=R_2=R_3=Ac$

Chart 1

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[3] K.R. Kirtikar and B.D. Basu, "Indian Medicinal Plants," The Indian Press, Allababad, 1918, p. 590.

[4] M.M. Lotlikar and M.R. Rajarama Rao, *J. Univ. Bombay*, **29**, 223 (1960-61) [*C.A.*, **58**, 9537*d* (1963)]; S.S. Gupta, *Indian J. Med. Res.*, **51**, 716 (1963) [*C.A.*, **60**, 6094*e* (1964)]; W. Sucrow, *Tetrahedron Lett.*, **1965**, 2217; V.S. Baldwa, C.M. Bhandari, A. Pangaria, and R.K. Goyal, *Upsala J. Med. Sci.*, **82**, 39 (1977) [*Planta Medica*, **34**, 280 (1978)].

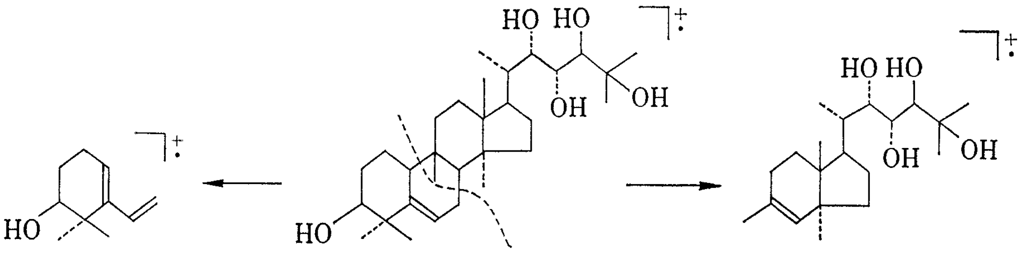
As a first step in chemical studies of the bitter principles of the fruit, the seed was investigated. This paper deals with the isolation and structure elucidation of two kinds of oligoglycosides of a cucurbitane derivative, named momordicosides A (I) and B (II).

The defatted methanol extractive of the seeds was partitioned between butanol and water and the latter layer, containing vicine (III),[5] was discarded. The butanol layer was subjected to successive column chromatographies and two compounds, I, $C_{42}H_{72}O_{15}\cdot 2H_2O$, mp 181—187° (dec.), $[\alpha]_D$ +1.05°, and II, $C_{47}H_{80}O_{19}\cdot 3/2H_2O$, mp 238—242° (dec.), $[\alpha]_D$ +6.15°, were isolated.

On mild methanolysis, I gave methyl glucoside and an aglycone (IV), while II furnished a product identical with I, methyl xyloside and glucoside, and IV, indicating II to be a xyloside of I. IV was assumed to retain its structure in glycosides I and II, since IV was also obtained on enzymatic hydrolysis of I, and the carbon-13 nuclear magnetic resonance (CMR) spectrum of IV was almost identical with those of I and II, except for the signals due to sugar moieties and those of the aglycone carbons affected by the glycoside linkage.

IV was formulated as $C_{30}H_{52}O_5$ based on the elementary analysis results and the molecular ion peak (M^+) observed at m/z 492 in the field desorption mass spectrum (FD-MS). The proton nuclear magnetic resonance (PMR) of IV exhibited the signals of seven tertiary (0.90 (×2), 0.94, 1.12, 1.40, 1.67 and 1.75 ppm) and one secondary (1.43 ppm) methyl groups along with four methines bearing hydroxyl groups (3.74, 4.07, 4.37 and 4.57 ppm) and one olefinic proton at 5.61 ppm as a broad doublet (J=*ca.* 4 Hz). The presence of four secondary and one tertiary hydroxyl groups was seen in the CMR spectrum of IV as five peaks between 70 and 76 ppm, four of which were transformed to doublets by off-resonance decoupling measurement, while one remained as a singlet. In the region from 34.8 to 49.2 ppm, four quaternary carbon signals were observed, and olefinic carbons were found at 143.0 (singlet) and 119.1 ppm (doublet).

Its molecular formula and the presence of one double bond, seven tertiary methyl groups, and four C–C bonded and one hydroxylated quaternary carbons, as described above, suggested IV to be a tetracyclic triterpenoid. The PMR and CMR patterns due to a proton and carbons of a double bond, respectively, were similar to those of cucurbit-5-ene derivatives,[6] and the EI-MS spectrum of IV showed peaks at m/z 152 and 340 which could be considered to be provided by the typical retro-Diels–Alder fragmentation of ring B of a cucurbit-5-ene derivative having one hydroxyl group in ring A.[6a,7]



m/z 152 m/z 492 m/z 340

Chart 2

IV was acetylated with Ac_2O and pyridine at room temperature to give a tetraacetate (V) and at 90° to give a pentaacetate (VI). The hydroxyl group acylable only on heating was tentatively located at C-25 of the cucurbitane nucleus, and the two singlets at 1.67 and 1.75 ppm in the PMR spectrum of IV were assigned to the 26- and 27-methyl groups.

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5) A. Bendich and G.C. Clements, *Biochem. Biophys. Acta*, **12**, 462 (1953).

6) *a*) R. Tschesche, G. Biernoth and G. Snatzke, *Ann.*, **674**, 196 (1964); *b*) Y. Yamada, K. Hagiwara, K. Iguchi, and Y. Takahashi, *Chemistry Letters*, **1978**, 319.

7) P. Tunmann, W. Gerner and G. Stapel, *Ann.*, **694**, 162 (1966).

The finding that IV afforded mono- (VII) and di- (VIII) acetonides, and the coupling patterns (δ 3.83 (d, $J=9$ Hz), δ 4.10 (dd, $J=7$, 9 Hz) and δ 4.36 (d, $J=7$ Hz)) of three protons on three carbinyl carbons of VIII, suggested that two glycol systems were adjacent to each other. When the monoacetonide (VII) was subjected to periodate oxidation, an aldehyde (IX) was obtained. An FD–MS spectrum of IX showed the $(M+H)^+$ ion peak at m/z 473, indicating that bond fission in VII took place between C-24 and -25. On the other hand, when IV was treated with periodic acid in methanol, the bond between C-22 and -23 was cleaved to give a mixture of an aldehyde (X) and its dimethyl acetal (XI) which retained one secondary hydroxyl group. Therefore, four hydroxyl groups were thought to be located at C-22, -23, -24 and -25.

The remaining one hydroxyl group was assumed to be at C-3, and this was confirmed by converting XI to an oxo derivative (XII) and further to the corresponding 2-hydroxy-1-en-3-one (XIII); the PMR spectrum of the latter showed the proton at C-1 at 6.12 ppm as a doublet ($J=3$ Hz), also supporting the presence of a proton at C-10.

Consequently, IV was presumed to be a cucurbit-5-ene-3,22,23,24,25-pentaol.

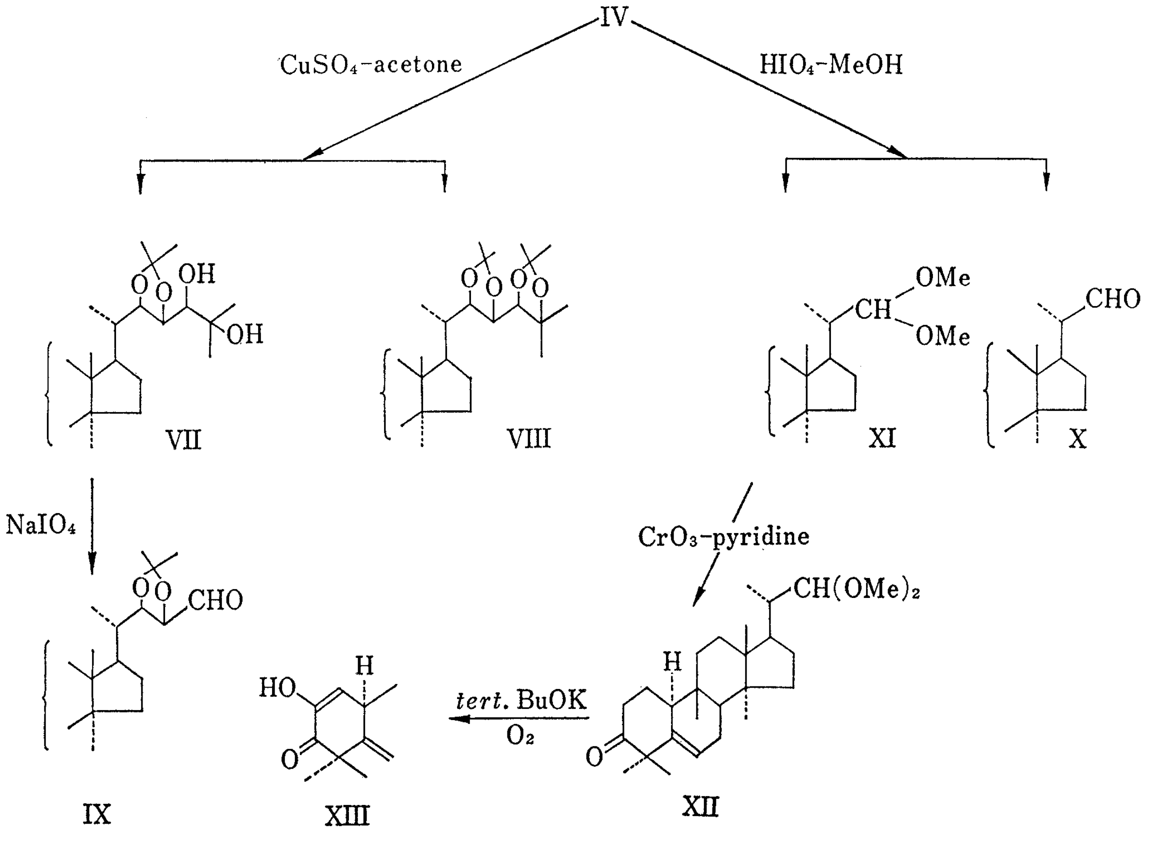

Chart 3

In order to confirm the cucurbitane framework and to determine the configurations of substituents, X-ray analysis of IV was carried out by the direct method. The final atomic parameters, bond lengths and bond angles for nonhydrogen atoms are given in Tables I, II and III, respectively, and an ORTEP drawing is shown in Fig. 1.

The aglycone was thus identified as cucurbit-5-ene-3β,22(S),23(R),24(R),25-pentaol (IV) or its enantiomer (IV′).

The CD spectrum of XII showed a negative Cotton curve ($[\theta]_{294}$ $-8030°$) indicating the

Table I. Fractional Atomic Coordinates and Anisotropic Thermal Parameters ($\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C 1	3347(4)	9863(9)	1631(5)	487(35)	375(33)	554(35)	7(32)	108(28)	−63(32)
C 2	3092(4)	10199(8)	473(5)	527(36)	361(36)	530(36)	60(30)	82(29)	90(29)
C 3	2739(4)	8579(9)	−104(4)	482(34)	541(41)	372(30)	−17(33)	108(25)	56(30)
C 4	3430(4)	7062(8)	93(4)	471(33)	485(37)	314(27)	6(30)	127(24)	−53(27)
C 5	3808(4)	6825(8)	1257(4)	412(31)	376(33)	376(28)	−28(28)	160(24)	−7(26)
C 6	3931(4)	5276(8)	1671(4)	490(34)	312(30)	423(31)	−115(27)	145(26)	−15(26)
C 7	4442(4)	4933(9)	2761(4)	499(35)	448(36)	437(31)	−120(33)	148(26)	93(30)
C 8	4976(4)	6470(8)	3294(4)	560(34)	300(28)	257(24)	−96(30)	147(22)	−2(25)
C 9	4428(4)	8183(8)	3054(4)	505(33)	396(34)	357(28)	−7(31)	168(24)	−67(28)
C 10	4118(4)	8476(7)	1858(4)	456(31)	243(29)	376(28)	−26(25)	146(23)	−49(24)
C 11	5013(4)	9737(9)	3513(4)	536(37)	472(37)	416(31)	22(34)	134(27)	−146(31)
C 12	6033(4)	9772(8)	3365(4)	522(35)	361(32)	425(30)	−20(31)	85(26)	−78(29)
C 13	6510(4)	8083(8)	3762(4)	540(33)	368(31)	258(24)	−15(31)	143(23)	24(26)
C 14	5998(4)	6542(8)	3134(4)	561(34)	283(28)	316(26)	−48(30)	110(24)	4(26)
C 15	6591(4)	5001(8)	3570(4)	621(38)	315(32)	381(30)	−77(31)	22(27)	−29(27)
C 16	7592(5)	5707(8)	3747(5)	632(42)	357(34)	516(37)	60(31)	71(31)	25(30)
C 17	7519(4)	7727(8)	3600(4)	511(33)	330(31)	309(26)	25(28)	91(24)	−11(25)
C 18	6490(4)	7938(10)	4956(4)	696(41)	557(40)	301(27)	−3(38)	202(27)	−23(32)
C 19	3564(4)	8052(11)	3603(4)	604(39)	691(46)	410(31)	−124(42)	208(28)	−77(36)
C 20	8312(4)	8735(8)	4245(4)	580(37)	370(32)	321(28)	18(31)	20(25)	−23(27)
C 21	8272(5)	10686(9)	3981(6)	642(45)	414(38)	733(47)	−19(35)	55(36)	−59(37)
C 22	9261(4)	7910(9)	4152(4)	515(34)	387(33)	372(28)	13(31)	−1(25)	−23(29)
C 23	9531(4)	7854(9)	3065(4)	494(35)	525(39)	362(28)	−39(33)	60(25)	1(31)
C 24	10232(4)	6374(9)	3010(4)	459(33)	467(37)	384(29)	−52(33)	12(24)	−45(31)
C 25	10655(4)	6356(11)	2003(4)	551(38)	710(48)	436(33)	−121(41)	178(28)	−83(37)
C 26	11320(5)	4821(13)	2011(7)	762(53)	846(61)	1012(61)	62(53)	469(47)	−159(57)
C 27	9920(5)	6364(13)	1027(5)	790(49)	888(58)	388(33)	−130(51)	184(32)	−50(42)
C 30	4261(4)	7443(9)	−465(4)	532(37)	572(42)	381(30)	70(33)	161(27)	51(31)
C 31	2962(4)	5409(9)	−402(5)	605(41)	514(41)	397(32)	5(34)	53(29)	−82(31)
C 32	6082(4)	6632(8)	1962(4)	571(34)	363(31)	254(24)	7(31)	93(23)	−43(26)
O 3	1872(3)	8125(7)	200(3)	456(23)	611(29)	496(23)	−26(25)	140(18)	1(25)
O 22	9986(3)	8805(7)	4835(3)	529(24)	749(34)	472(27)	66(26)	−68(20)	−118(25)
O 23	9925(3)	9491(7)	2869(4)	793(33)	482(30)	676(30)	−42(27)	193(25)	78(26)
O 24	9785(3)	4772(6)	3097(3)	593(26)	493(27)	498(24)	−34(25)	144(20)	−24(23)
O 25	11184(3)	7944(7)	2035(3)	605(28)	745(34)	659(28)	−243(30)	238(23)	−84(30)
O W	9137(4)	2213(7)	1658(4)	904(38)	687(38)	645(31)	−26(32)	−135(27)	121(29)

The anisotropic thermal parameters are expressed in the form: $\exp[-2\pi(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$.
Standard deviation for the last digit is given in parentheses.

Table II. Bond Lengths and Their Standard Deviations (Å)

C 1–C 2	1.518(9)	C 13–C 14	1.569(9)
C 1–C 10	1.553(9)	C 13–C 17	1.556(9)
C 2–C 3	1.512(9)	C 13–C 18	1.567(10)
C 3–C 4	1.546(9)	C 14–C 15	1.530(9)
C 3–O 3	1.439(9)	C 14–C 32	1.556(9)
C 4–C 5	1.540(9)	C 15–C 16	1.551(9)
C 4–C 31	1.545(9)	C 16–C 17	1.577(9)
C 4–C 30	1.550(10)	C 17–C 20	1.535(9)
C 5–C 6	1.315(8)	C 20–C 21	1.547(10)
C 5–C 10	1.531(8)	C 20–C 22	1.557(9)
C 6–C 7	1.519(9)	C 22–C 23	1.535(10)
C 7–C 8	1.530(9)	C 22–O 22	1.450(9)
C 8–C 9	1.556(9)	C 23–C 24	1.550(10)
C 8–C 14	1.551(8)	C 23–O 23	1.434(9)
C 9–C 10	1.570(9)	C 24–C 25	1.544(11)
C 9–C 11	1.543(10)	C 24–O 24	1.417(8)
C 9–C 19	1.559(11)	C 25–C 26	1.537(13)
C 11–C 12	1.543(10)	C 25–C 27	1.529(13)
C 12–C 13	1.533(9)	C 25–O 25	1.452(10)

Standard deviation for the last digit is given in parentheses.

Table III. Bond Angles and Their Standard Deviations(Å)

C 2–C 1–C 10	111.2(5)	C 10–C 9–C 11	109.1(5)	C 13–C 17–C 16	101.9(5)
C 1–C 2–C 3	111.3(5)	C 10–C 9–C 19	110.0(5)	C 13–C 17–C 20	119.4(5)
C 2–C 3–C 4	112.6(6)	C 11–C 9–C 19	108.5(6)	C 16–C 17–C 20	114.1(5)
C 2–C 3–O 3	108.3(5)	C 1–C 10–C 5	109.5(5)	C 17–C 20–C 21	112.2(5)
C 4–C 3–O 3	110.8(5)	C 1–C 10–C 9	111.9(5)	C 17–C 20–C 22	111.0(5)
C 3–C 4–C 5	112.1(5)	C 5–C 10–C 9	113.8(5)	C 21–C 20–C 22	112.6(5)
C 3–C 4–C 31	109.0(5)	C 9–C 11–C 12	117.2(6)	C 20–C 22–C 23	117.0(6)
C 3–C 4–C 30	108.9(5)	C 11–C 12–C 13	110.0(5)	C 20–C 22–O 22	109.5(5)
C 5–C 4–C 31	112.3(5)	C 12–C 13–C 14	108.6(5)	C 23–C 22–O 22	107.9(5)
C 5–C 4–C 30	107.5(5)	C 12–C 13–C 17	119.8(5)	C 22–C 23–C 24	109.8(6)
C 30–C 4–C 31	106.9(5)	C 12–C 13–C 18	108.4(5)	C 22–C 23–O 23	108.2(6)
C 4–C 5–C 6	121.1(6)	C 14–C 13–C 17	100.4(5)	C 24–C 23–O 23	110.7(6)
C 4–C 5–C 10	115.8(5)	C 14–C 13–C 18	112.4(5)	C 23–C 24–C 25	114.2(6)
C 6–C 5–C 10	122.8(5)	C 17–C 13–C 18	107.2(5)	C 23–C 24–O 24	108.8(6)
C 5–C 6–C 7	123.9(6)	C 8–C 14–C 13	110.4(5)	C 25–C 24–O 24	108.4(6)
C 6–C 7–C 8	115.4(5)	C 8–C 14–C 15	115.2(5)	C 24–C 25–C 26	110.2(7)
C 7–C 8–C 9	111.2(5)	C 8–C 14–C 32	111.6(5)	C 24–C 25–C 27	112.5(7)
C 7–C 8–C 14	113.8(5)	C 13–C 14–C 15	101.8(5)	C 24–C 25–O 25	104.8(6)
C 9–C 8–C 14	115.0(5)	C 13–C 14–C 32	111.9(5)	C 26–C 25–C 27	111.7(7)
C 8–C 9–C 10	112.2(5)	C 15–C 14–C 32	105.6(5)	C 26–C 25–O 25	108.5(7)
C 8–C 9–C 11	110.4(5)	C 14–C 15–C 16	104.4(5)	C 27–C 25–O 25	108.9(7)

Standard deviation for the last digit is given in parentheses.

presence of a 10α-hydrogen atom and a 5,6-double bond.[8)]

Thus, the absolute structure was established as IV.

Momordicoside A (I) showed the $(M+Na)^+$ peak at m/z 839 in the FD-MS spectrum, and the anomeric carbon signals at 105.2 and 106.9 ppm in the CMR spectrum. The EI-MS spectrum of its acetate (XIV) showed a fragment peak (m/z 619) due to an acetylated biose moiety. These data suggest that the sugar moiety of I is composed of two moles of glucose. The signals in the CMR spectrum ascribable to the sugar carbons were quite similar to those of pregnenolone gentiobioside.[10)]

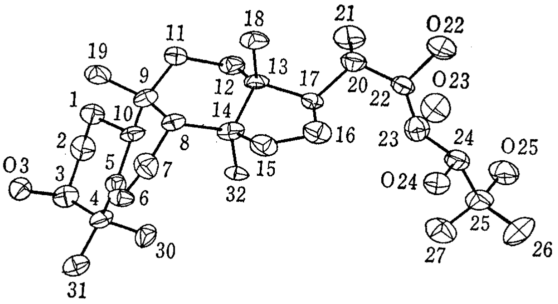

Fig. 1. An ORTEP Drawing of the Molecular Structure

When I was methylated in tetrahydrofuran with NaH and CH_3I, two methylates (XV and XVI) were obtained. Methanolysis of either XV or XVI furnished equal amounts of methyl pyranosides of 2,3,4,6-tetra-O-methyl glucose and 2,3,4-tri-O-methyl glucose. The linkage between the two glucose units as well as that to the aglycone were regarded as β in view of the coupling constants (*ca.* 7 Hz) of the two anomeric protons in the PMR spectrum of XV. The aglycones provided by methanolysis of XV and XVI were 25,26-anhydro- (XVII), 22,25-anhydro(XVIII) and 22,23,24,25-tetra-O-methyl (XIX) derivatives from the former, and XVII, XVIII and 22,23,24-tri-O-methyl ether (XX) from the latter. Thus, XV is the permethylate of I, while XVI has a free hydroxyl group at C-25.

Sugar linkage with the hydroxyl group at C-3 in I was confirmed by its CMR spectrum, in which a downfield shift of the C-3 signal compared with that in IV was observed, and by the result that XIX was afforded by methanolysis of XV.

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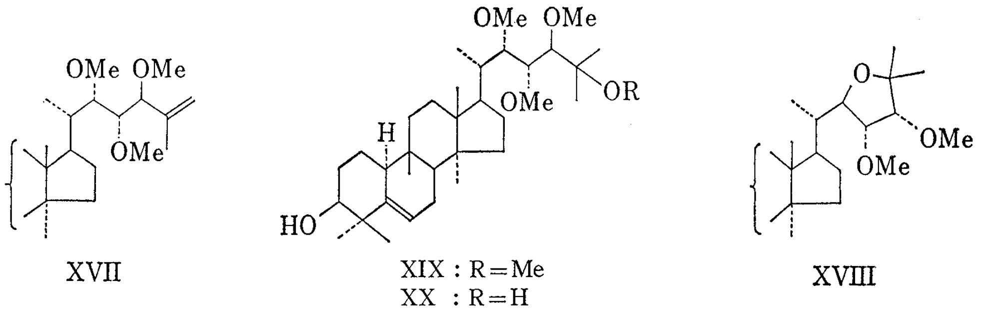
8) Alnusenone, a pentacyclic triterpene having a 10α-hydrogen, a 5,6-double bond and a 3-keto group gives a negative CD curve ($[\theta]_{295}$ $-3630°$), while 4,4-dimethylcholest-5-en-3-one and 17β-acetoxy-4,4-dimethyl-19-norlanost-5-en-3-one show positive CD curves ($[\theta]_{294}$ $+5148°$ and $[\theta]_{307}$ $+5752°$, respectively).[9)] These CD data were referred to in the determination of the cucurbit-5-ene nucleus of gratiogenin.[6a)]

9) P. Witz, H. Hermann, J-M. Lehn and G. Ourisson, *Bull. Soc. Chim. France*, **1963**, 1101.

10) T. Yamauchi, M. Hara and K. Mihashi, *Phytochemistry*, **11**, 3345 (1972).



XVII

XIX : R=Me
XX : R=H

XVIII

Chart 4

Accordingly, I was concluded to be the 3-O-β-gentiobioside of IV.

On comparison of the FD-MS spectra and the molecular formulae of I and II, the sugar moiety of the latter appeared to be composed of two moles of glucose and one of xylose. The EI-MS spectrum of II-acetate (XXI) showed peaks at m/z 331 and 259, corresponding to the pyronium ions originated from the terminal acetylated glucose and xylose residues, indicating a branched chain trisaccharide structure. II-Permethylate (XXIIa) was subsequently methanolyzed and the resulting methylated monosaccharides were identified by GLC as methyl pyranosides of 2,3,4-tri-O-methyl xylose, 2,3,4,6-tetra-O-methyl glucose and 2,3-di-O-methyl glucose. Since I was formed by partial hydrolysis of II, the xylose unit in II should be linked to the hydroxyl group at C-4 of the glucose combined with the aglycone. The mode of linkage of the xylose unit was determined as β judging from the coupling constant (6 Hz) of its anomeric proton signal in the PMR spectrum of XXIIa.

Thus, II is the 3-O-β-D-xylopyranosyl-(1→4)-[β-D-glucopyranosyl (1→6)]-β-D-glucopyranoside of IV.

More than thirty cucurbitane derivatives have so far been isolated from plants, mainly of Cucurbitaceae and also of Primulaceae,(11) Cruciferae,(12) Begoniaceae(13) and Datiscaceae.(14) They are, in general, highly oxygenated and the oxygen functions are distributed in the nucleus and side chain (C-3 and C-11 being invariably oxygenated).

The aglycone (IV) of momordicosides A (I) and B (II) is also a typical cucurbitane derivative, but is unusual in that four of the five hydroxyl groups are located in the side chain and in that there is no oxygen function at C-11.

Experimental(15)

Extraction and Isolation of I, II and III——Seeds (3.34 kg) of *Momordica charantia* L. were crushed and percolated successively with MeOH (20 l) and MeOH–H_2O (1: 1) (20 l). The MeOH solution was concentrated under reduced pressure to 1/10 volume, and repeatedly extracted with hexane to remove lipids. The MeOH solution was concentrated to dryness, suspended in water and extracted with BuOH. The BuOH solution was concentrated to dryness to give a light brown powder (55 g). This was repeatedly chromato-

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15) Instruments and materials used in this work were as follows: Yanaco micromelting point apparatus (melting points), Shimadzu UV-200S double beam spectrophotometer (UV spectra), Hitachi grating infrared spectrophotometer, model EPI-G3 (IR spectra), JASCO DIP-4 digital polarimeter (specific rotations), JASCO J-20 automatic recording spectropolarimeter (CD spectra), JEOL JNM PS-100 (100 MHz) and Hitachi R-22 (90 MHz) spectrometers (PMR spectra), JEOL JMN FX-100 (25 MHz) spectrometer (CMR spectra), Shimadzu GC-3BF gas chromatograph (GLC), JEOL JMS-01SG mass spectrometer (EI-MS spectra), JEOL D-300 FD mass spectrometer (FD-MS spectra), Kieselgel 60 (70—230 mesh) (E. Merck) (column chromatography), precoated Kieselgel 60 F_{254} plates (E. Merck) (TLC). Melting points are uncorrected. PMR and CMR spectra were measured in pyridine-d_5 unless otherwise stated, and chemical shifts are expressed in the δ-scale using tetramethylsilane as an internal standard (s, singlet; br, broad; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet).

graphed on silica gel (50—100 times the weight of material) using $CHCl_3$–MeOH–H_2O (70: 25: 3) as an eluent to give I (4.3 g) and II (0.3 g).

I: colorless needles from MeOH, mp 181—187° (dec.), $[\alpha]_D^{20^\circ}$ +1.05° (c=0.96, $CHCl_3$–MeOH (2: 1)), FD–MS m/z: 839 $(M+Na)^+$, 855 $(M+K)^+$. *Anal.* Calcd for $C_{42}H_{72}O_{15}\cdot 2H_2O$: C, 59.13; H, 8.98. Found: C, 58.95; H, 8.85. CMR: olefinic carbons: 143.27(s), 118.66 (d); oxygen-bearing carbons: 106.91(d), 105.16(d), 87.27(d), 78.41(d), 77.33(d), 75.24, 75.14, 74.41(s), 72.41, 71.63(d), 71.19, 70.12, 62.72(t); quaternary carbons: 49.12, 46.78, 41.66, 34.70.

II: colorless needles from MeOH–$CHCl_3$, mp 238—242° (dec.), $[\alpha]_D^{20^\circ}$ +6.15° (c=0.98, $CHCl_3$–MeOH (2: 1)), FD–MS m/z: 971 $(M+Na)^+$. *Anal.* Calcd for $C_{47}H_{80}O_{19}\cdot 3/2H_2O$: C, 57.83; H, 8.57. Found: C, 57.60; H, 8.43. CMR: olefinic carbons: 142.85(s), 118.48(d); oxygen-bearing carbons: 106.58(d), 104.82(d), 87.19(d), 79.98(d), 79.51, 78.10(d), 76.11, 74.94, 74.71, 74.24(s), 72.25, 71.48, 71.07, 70.66, 68.38, 67.38, 62.64(t); quaternary carbons: 49.04, 46.70, 41.60, 34.63.

The aqueous layer from the BuOH–H_2O extraction of the defatted MeOH extractives and the MeOH–H_2O extract were combined and concentrated. On standing at room temperature colorless needles (11 g) were separated out, and these were recrystallized from water to give III: colorless needles, mp 250—255° (dec.), $[\alpha]_D^{25^\circ}$ −13.5° (c=2.15, 0.1% NaOH). *Anal.* Calcd for $C_{10}H_{16}N_4O_7\cdot 1/2H_2O$: C, 38.33; H, 5.43; N, 17.89. Found: C, 38.66; H, 5.47; N, 17.95. UV $\lambda_{max}^{0.5\,N\,HCl}$ nm (ε): 273 (15800), $\lambda_{max}^{H_2O}$ nm (ε): 275 (12770), 210 (20400), $\lambda_{max}^{0.1\,N\,NaOH}$ nm (ε): 268 (9700), 235 (5624), 217 (8500). CMR (1 N KOH): base moiety, 170.3, 160.9, 158.8, 118.6; sugar moiety, 108.0 (1′), 78.6 (3′), 77.9 (5′), 74.7 (2′), 71.5 (4′), 62.6 (6′). IR (KBr): superimposable on the spectrum of vicine[16] isolated from faba beans (*Vicia faba* L.) according to the method of Lin *et al.*[17]

Methanolysis of I, Identification of the Component Sugar and Isolation of the Aglycone (IV)——A solution of I (610 mg) in 1 N HCl–MeOH (20 ml) was stirred for 5 days at room temperature then neutralized with Ag_2CO_3. The precipitates were filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (160 g). Elution with 3% MeOH–$CHCl_3$ gave an aglycone (223 mg), which was crystallized from MeOH to give colorless needles (IV): mp 193—195° $[\alpha]_D^{20^\circ}$ +48.1° (c=0.94, $CHCl_3$–MeOH (2: 1)). FD–MS m/z: 492 (M^+). *Anal.* Calcd for $C_{30}H_{52}O_5\cdot 1/2H_2O$: C, 71.86; H, 10.58. Found: C, 72.04; H, 10.79. PMR: 0.90 (6H, s, $\geqslant C{-}C\underline{H}_3\times 2$), 0.94 (3H, s, $\geqslant C{-}C\underline{H}_3$), 1.12 (3H, s, $\geqslant C{-}C\underline{H}_3$), 1.40 (3H, s, $\geqslant C{-}C\underline{H}_3$), 1.43 (3H, d, J=6 Hz, $>CH{-}C\underline{H}_3$), 1.67, 1.75 (3H each, s, $HO{-}\underset{|}{C}(C\underline{H}_3)_2$), 3.74 (H, br s, $>C\underline{H}{-}OH$), 4.07 (H, d, J=9 Hz, $-C\underline{H}(OH){-}CH(OH){-}$), 4.37 (H, d, J=9 Hz, $-CH(OH){-}C\underline{H}(OH){-}$), 4.57 (H, d, J=4 Hz, $>CH{-}OH$), 5.61 (H, br d, J=4 Hz, $>C{=}C\underline{H}{-}$). CMR: olefinic carbons: 143.02 (s), 119.12(d); oxygen-bearing carbons: 75.94(d), 75.23(d), 74.30(s), 72.30(d), 71.13(d); quaternary carbons: 49.16, 46.82, 41.60, 34.80. EI–MS m/z: 492 (M^+), 474 $(M^+{-}H_2O)$, 340, 322, 177, 159, 163, 152, 134, 59.

Elution with 25% MeOH–$CHCl_3$ gave resinous methyl glycoside (160 mg) ($[\alpha]_D^{25^\circ}$ +93.1° (c=1.23, MeOH)). Its PMR spectrum exhibited two methoxyl proton signals at 3.46 and 3.61 ppm in a ratio of 2: 1 and anomeric proton signals at 4.73 (d, J=7 Hz) and 5.17 ppm (d, J=4 Hz) (methoxyl proton signals: methyl α-D-glucopyranoside, 3.46: β-anomer, 3.61 ppm. Anomeric proton signals: methyl α-D-glucopyranoside, 5.17 (d, J=4 Hz); β-anomer, 4.73 ppm (d, J=7 Hz)). The methyl glycoside was acetylated in the usual manner and examined by GLC.[18] It gave two peaks with retention times (4.6 and 5.2 min) identical with those of methyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside and its β-anomer.

Enzymatic Hydrolysis of I——I (80 mg) was suspended in water (8 ml) and cellulase (Type I, Sigma Chemical Co.) (80 mg) was added. The mixture was shaken for a week at 38°. The reaction mixture was extracted with $CHCl_3$ and then with BuOH. Both extracts were combined and chromatographed on silica gel (15 g). The fraction eluted with 3% MeOH–$CHCl_3$ gave the aglycone (33 mg) as colorless needles (crystallized from MeOH), identical with IV (IR and mixed mp).

Methanolysis of II, Identification of the Component Sugars and Isolation of Momordicoside A (I) and the Aglycone (IV)——II (660 mg) was dissolved in 1 N HCl–MeOH (20 ml) and stirred for 5 hr at room temperature. The reaction mixture was neutralized with Ag_2CO_3 and worked up in the same way as for I. The product was treated with 15% acetone–H_2O and the insoluble material (550 mg) was chromatographed on silica gel (70 g), using $CHCl_3$–MeOH–H_2O (70: 25: 3) as an eluent, to give Fr. 1 (143 mg), Fr. 2 (170 mg) and Fr. 3 (170 mg). Fr. 1 was further chromatographed on silica gel (30 g) (eluent, 3% MeOH–$CHCl_3$) to provide a thin-layer-chromatographically homogeneous compound, which was crystallized from MeOH to give colorless needles (46 mg): mp 192—195°. The IR spectrum was superimposable on that of IV and the melting point was not depressed on admixture with IV. Fr. 2 was crystallized from MeOH–H_2O to give colorless needles (94 mg): mp 180—188° (dec.). This product gave the same IR and CMR spectra as I. Fr. 3 gave II on recrystallization.

The 15% acetone-soluble substance (122 mg) showed two spots on TLC and their *Rf* values were identical with those of methyl α-D-xylopyranoside (*Rf*: 0.46, $CHCl_3$–MeOH–H_2O (70: 35: 5)) and methyl α-D-glucopyranoside (*Rf*: 0.32). This mixture was subjected to column chromatography (silica gel, 11 g; $CHCl_3$–

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[16] Reported for vicine: mp 243—244° (dec.), $[\alpha]_D^{26^\circ}$ −11.7°, UV $\lambda_{max}^{0.1\,N\,HCl}$ nm (ε): 274 (16400). (Merck Index.)

[17] J.Y. Lin and K.H. Ling, *T'ai-wan I Hsueh Hui Tsa Chih*, **61**, 484 (1962) [*C.A.*, **65**, 4143*g* (1966)].

[18] 5% 1,4-butanediol succinate on Shimalite W; 2.1 m × 3 mmϕ; N_2 carrier gas at 1 kg/cm^2; 220°.

MeOH–H_2O (70: 25: 3)) to give two methyl glycosides. The less polar one (27 mg) showed $[\alpha]_D^{25^\circ}$ +127.6° (c=1.34, MeOH)[19] and its PMR spectrum exhibited methoxyl proton signals at 3.40 and 3.58 ppm (ratio 3: 1). It was acetylated and subjected to GLC,[18] giving two peaks with t_R 1.60 and 1.80 min (methyl α-D-xylopyranoside triacetate, t_R 1.55; β-anomer, 1.80). In the same way, the polar methyl glycoside was identified as a mixture of methyl α-D-glucopyranoside and its β-anomer.

Acetylation of IV——i) IV (20 mg) was dissolved in 0.6 ml of Ac_2O–pyridine (1: 1) and the solution was stirred for 15 hr at room temperature. The solution was then evaporated to dryness and the residue was chromatographed on silica gel (6 g) (4% acetone–benzene) to give a tetraacetate (V) (7 mg): fine needles (from acetone–benzene), mp 178—182°. PMR: 1.48 (6H, s, HO–$\underset{|}{\mathrm{C}}$(C$\underline{\mathrm{H}}_3$)$_2$), 2.00 (3H, s, –OAc), 2.12 (6H, s, –OAc × 2), 2.18 (3H, s, –OAc), 4.91 (H, perturbed t, >C$\underline{\mathrm{H}}$–OAc), 5.46 (H, d, J=7 Hz, >C$\underline{\mathrm{H}}$–OAc), 5.49 (H, m, >C=C$\underline{\mathrm{H}}$–), 5.71 (H, br s, >C$\underline{\mathrm{H}}$–OAc), 6.12 (H, d, J=7 Hz, >C$\underline{\mathrm{H}}$–OAc). CMR: olefinic carbons: 141.95(s), 119.44(d); oxygen-bearing carbons: 78.85(d), 76.65(d), 73.29(d), 71.58(s), 69.15(d); quaternary carbons: 49.12, 46.93, 39.91, 34.74; acetyl carbonyl carbons: 170.65, 170.56, 170.36, 170.17. EI–MS m/z: 660 (M^+), 600 ($M^+ -$ AcOH), 466, 406, 194, 163, 134.

ii) IV (50 mg) in 1 ml of Ac_2O–pyridine (1: 1) was heated at 90° for 6 hr. The solvent was removed and the residue was chromatographed on silica gel (20 g) (2.5% acetone-benzene) to give a pentaacetate (VI) (31 mg): colorless needles (from MeOH), mp 104—107°. *Anal.* Calcd for $C_{40}H_{62}O_{10}\cdot H_2O$: C, 66.64; H, 8.95. Found: C, 66.50; H, 8.73. PMR: 1.65, 1.69 (3H each, s, AcO–$\underset{|}{\mathrm{C}}$(C$\underline{\mathrm{H}}_3$)$_2$), 2.04 (6H, s, –OAc × 2), 2.16 (3H, s, –OAc), 2.18 (3H, s, –OAc), 2.21 (3H, s, –OAc), 4.92 (br s, >C$\underline{\mathrm{H}}$–OAc, partially overlapping with an H_2O signal), 5.54 (2H, br s, >C–C$\underline{\mathrm{H}}$– and >C$\underline{\mathrm{H}}$–OAc), 5.81 (H, d, J=8 Hz, >C$\underline{\mathrm{H}}$–OAc), 6.01 (H, d, J=8 Hz, >C$\underline{\mathrm{H}}$–OAc). CMR: olefinic carbons: 141.68(s), 119.18(d); oxygen-bearing carbons: 81.97(s), 78.63(d), 73.42(d), 72.71(d), 68.61(d); quaternary carbons: 49.04, 46.87, 39.79, 34.69; acetyl carbonyl carbons: 170.16, 169.98, 169.51. EI–MS m/z: 702 (M^+), 642 ($M^+ -$ AcOH), 508, 448, 163, 134.

Formation of Mono- (VII) and Diacetonides (VIII)——A mixture of IV (60 mg) and anhydrous $CuSO_4$ (160 mg) in anhydrous acetone (2.3 ml) was stirred at room temperature for 19 hr. The mixture was then diluted with $CHCl_3$ and filtered, and the filtrate was concentrated. The residue (53 mg) was repeatedly chromatographed on silica gel (200 times the weight of material), using 1% MeOH–$CHCl_3$ as an eluent, to give diacetonide (VIII) (7 mg) and monoacetonide (VII) (41 mg). VIII: colorless needles (from MeOH), mp 208—209.5°. PMR: 3.75 (H, br s, >C$\underline{\mathrm{H}}$–OH), 3.83 (H, d, J=9 Hz), 4.10 (H, dd, J=7, 9 Hz), 4.36 (H, d, J=7 Hz), 5.69 (br d, J=5 Hz, >C=C$\underline{\mathrm{H}}$–). EI-MS m/z; 572 (M^+), 557 ($M^+ - CH_3$), 554 ($M^+ - H_2O$), 443, 420 ($M^+ -$ 152), 405 ($M^+ - CH_3 -$ 152), 163, 152, 134. VII: colorless needles (acetone–benzene), mp 176—178°. *Anal.* Calcd for $C_{33}H_{56}O_5\cdot 3/2H_2O$: C, 70.80; H, 10.62. Found: C, 70.68; H, 10.25. PMR: 3.74 (H, br s, >C$\underline{\mathrm{H}}$–OH), 3.83 (H, d, J=9 Hz), 4.32 (H, dd, J=6, 9 Hz), 4.61 (H, d, J=6 Hz), 5.61 (H, d, J=4 Hz). CMR: olefinic carbons: 142.93(s), 119.00(d); oxygen-bearing carbons: 107.62(s), 84.77(d), 79.03(d), 77.47(d), 75.82(d), 73.05(s); quaternary carbons: 49.22, 46.69, 41.53, 34.72. EI–MS m/z: 532 (M^+), 517 (M^+–CH_3), 443, 380 ($M^+ -$ 152), 362 (380—H_2O), 163, 152, 134.

Periodate Oxidation of VII——VII (1.8 mg) was dissolved in 0.1 ml of MeOH, and 10% $NaIO_4$ aqueous solution (10 μl) was added. The mixture was stirred in the dark for 40 hr, then diluted with water. The precipitates were collected by centrifugation and recrystallized from MeOH to give colorless needles (IX): mp 109—115°. FD–MS m/z: 473 $(M+H)^+$. Calcd for $C_{30}H_{48}O_4$: 472.

Periodic Acid Oxidation of IV——IV (261 mg) in MeOH (16 ml) was mixed with 25% HIO_4 aqueous solution (1.6 ml) and the whole was stirred in the dark for 2 days. Precipitates were centrifuged off and the supernatant was diluted with water then extracted with $CHCl_3$. The precipitates and $CHCl_3$ extract were combined and chromatographed on a silica gel (100 g) column, eluting with 12% AcOEt–hexane, to give an aldehyde (X) (32 mg) and a dimethyl acetal (XI) (150 mg). X: colorless needles (MeOH), mp 156—159°. PMR: 3.74 (H, br s, >C$\underline{\mathrm{H}}$–OH), 5.64 (H, br d, J=6 Hz, >C=C$\underline{\mathrm{H}}$–), 9.70 (H, d, J=3 Hz, >CH–C$\underline{\mathrm{H}}$O). CMR: an aldehydic carbon: 204.49(d); olefinic carbons: 142.81(s), 118.95(d); oxygen-bearing carbon: 75.82(d); quaternary carbons: 48.87, 46.93, 41.45, 34.86. EI–MS m/z: 372 (M^+), 357 ($M^+ - CH_3$), 354 ($M^+ - H_2O$), 339 (354 − H_2O), 220 ($M^+ -$ 152), 205 (220–CH_3), 152, 134. XI: colorless needles (MeOH), mp 155—157°. *Anal.* Calcd for $C_{27}H_{46}O_3\cdot H_2O$: C, 74.26; H, 11.08. Found: C, 74.35; H, 11.03. PMR: 3.37, 3.45 (3H each, s, –CH(OC$\underline{\mathrm{H}}_3$)$_2$), 3.72 (H, br s, >C$\underline{\mathrm{H}}$–OH), 4.22 (H, d, J=1.5 Hz, >CH–C$\underline{\mathrm{H}}$(OCH$_3$)$_2$), 5.64 (H, br d, J=5 Hz, >C=C$\underline{\mathrm{H}}$–). CMR: olefinic carbons: 143.09(s), 119.00(d); oxygen-bearing carbons: 109.34(d), 75.88(d), 56.72(q), 55.61(q); quaternary carbons: 49.10, 46.58, 41.60, 34.80. EI–MS m/z: 418 (M^+), 386 ($M^+ -$ MeOH), 368 (386–H_2O), 266 ($M^+ -$ 152), 234 (266–MeOH), 152, 134, 75 (–CH(OMe)$_2^+$).

Oxidation of Dimethyl Acetal (XI) with CrO_3——XI (160 mg) was added to 3% CrO_3 pyridine solution (5.6 ml) and the whole was stirred at room temperature for 20 hr. $CHCl_3$ (24 ml) was then added to the reaction mixture, and precipitates were collected by filtration and washed with $CHCl_3$. The filtrate and washings were combined and shaken with water. The $CHCl_3$ layer was dried with anhydrous Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (90 g), using $CHCl_3$ as an eluent, to give a ketone (80 mg), which was crystallized from MeOH to afford colorless plates (XII): mp 158—160°. PMR:

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19) Reported for methyl α-D-xylopyranoside: +153.9° (H_2O) [*J. Am. Chem. Soc.*, **47**, 265 (1925)].

3.40, 3.48 (3H each, s, $-CH(O\underline{Me})_2$), 4.24 (H, d, $J=3$ Hz, $-C\underline{H}(OMe)_2$), 5.64 (H, d, $J=6$ Hz, $>C=C\underline{H}-$). CMR: carbonyl carbon: 212.40(s); olefinic carbons: 142.91(s), 119.88(d); dimethyl acetal carbons: 109.22(d), 56.66(q), 55.61(q); quaternary carbons: 50.86, 48.93, 46.46, 35.04. EI-MS *m/z*: 416 (M^+), 384 (M^+-MeOH), 353 (384–OCH_3), 313, 266, 234, 219, 163, 150, 75. CD ($c=0.43\times10^{-3}$ g/ml, dioxane) $[\theta]^{20°}$ (nm): 0° (326), −4530° (313), −7740° (303), −7530° (300), −8030° (294), −1930° (265), 0° (244).

Air Oxidation of XII, Formation of Diosphenol (XIII)——XII (30 mg) was dissolved in 1 N *tert*-BuOK in *tert*-BuOH (2 ml), and oxygen gas was bubbled through the solution. The mixture was stirred at room temperature until the spot of XII disappeared on TLC. After neutralization with 1 N HCl–MeOH, and evaporation to dryness *in vacuo*, the residue was treated with $CHCl_3$. The soluble portion was chromatographed on silica gel (8 g) (eluent, 10% AcOEt–hexane) to give a diosphenol (XIII) (6.5 mg), which was crystallized from hexane containing a small amount of acetone to give colorless needles, mp 173—176°. $FeCl_3$ test in EtOH: brown. PMR ($CDCl_3$): 3.39, 3.44 (3H each, s, $-CH(O\underline{Me})_2$), 4.14 (H, d, $J=2$ Hz, $-C\underline{H}(OMe)_2$), 5.70 (H, m, $>C=C\underline{H}-$), 5.86 (H, s, exchangeable with D_2O, $C_2-O\underline{H}$), 6.12 (H, d, $J=3$ Hz, C_1-H). EI-MS *m/z*: 430 (M^+), 398 (M^+-MeOH), 366 (398–MeOH), 266, 234 (266–MeOH), 164, 163, 75. UV $\lambda_{max}^{Dioxane}$ nm (ε): 212 (6290), 271 (7320). CD ($c=0.17\times10^{-3}$ g/ml, dioxane) $[\theta]^{21°}$ (nm): 0° (370), −2300° (360), −8100° (350), −21000° (330), −25300° (321), −22300° (313), 0° (289).

X-Ray Analysis of IV——Crystal data: $C_{30}H_{52}O_5\cdot H_2O$ (M.W. = 510.762), monoclinic (from CH_3CN-H_2O), space group $P2_1$, $a=14.697(3)$ Å, $b=7.742(2)$ Å, $c=13.053(3)$ Å, $\beta=99.41(2)°$, $V=1465.3(6)$ Å^3, $Z=2$, $D_{calcd}=1.16$ g/cm^3.

A crystal with approximate dimensions of 0.1 × 0.2 × 0.35 mm was mounted on a SYNTEX P$\bar{1}$ fully automated four-circle diffractometer, and the lattice constants were derived by a least-squares fitting of 15 reflections. The intensities of all 3621 unique reflections having $2\theta\leq55°$ were measured using graphite-monochromated Mo Kα radiation ($\lambda=0.71069$ Å) and the $2\theta-\theta$ scan technique. After correction by the usual Lorentz and polarization factors, the intensities were converted to normalized structure factors. The phases were assigned to the 270 largest E-values ($E\geq1.7$) by a multisolution, weighted tangent formula approach.[20] The E-synthesis from the phase set having the least R-value showed 33 plausible nonhydrogen atoms. The complete structure (less hydrogens and with one molecule of water) was obtained by successive D-Fourier synthesis. Hydrogen atoms other than the five hydroxyl protons were located on the basis of geometrical considerations.

Block-diagonal least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogens reduced the R-factor to the final value of 0.059 for the 2180 observed reflections ($I>2.3\ \sigma_I$).

An ORTEP drawing of the structure, the final atomic parameters, bond lengths, and bond angles for nonhydrogen atoms are shown in Fig. 1 and Tables I, II and III, respectively.

All the calculations were performed on a FACOM M-190 computer at the Computer Center of Kyushu University using the UNICS II[21] and MULTAN[20] programs.

Acetylation of I——A solution of I (104 mg) in Ac_2O–pyridine (1 : 1) (2 ml) was heated on a boiling water bath for 16 hr. The mixture was then evaporated down under an air stream, and the residue (138 mg) was chromatographed on a silica gel (40 g) column, eluting with benzene–acetone mixture (4% acetone→20%), to give two compounds. The less polar one (55 mg) was crystallized from EtOH to give colorless needles (XIV): mp 148—152°. CMR: olefinic carbons: 142.09(s), 118.83(d); oxygen-bearing carbons: 101.98(d), 101.02(d), 86.66(d), 81.97(s), 73.77, 73.42, 72.71, 72.30, 72.07, 71.78, 69.67, 68.91, 68.61, 62.61(t); quaternary carbons: 49.04, 46.87, 41.19, 34.80; acetyl carbonyl carbons were omitted. EI-MS *m/z*: 619, 331, 271 (331–AcOH), 582, 448, 134.

Methylation of I——A mixture of I (600 mg) in freshly distilled anhydrous tetrahydrofuran (7 ml) and sodium hydride (350 mg) was sonicated for 10 min. CH_3I (7 ml) was added to the mixture and the whole was stirred for 25 hr at room temperature. Precipitates were filtered off and washed with $CHCl_3$. The filtrate and washings were combined and concentrated under reduced pressure to give a thick syrup (818 mg). Chromatography on silica gel (125 g) using 15% acetone–benzene gave two compounds: XV (196 mg) and XVI (184 mg), both as syrups. XV and XVI exhibited similar PMR spectra except for the signals of two methyl groups at C-25 (XV, 1.30 ppm; XVI, 1.46 ppm) and an additional OCH_3 at 3.26 ppm in XV.

Methanolysis of XV and XVI, Identification of Methylated Sugars and Isolation of XVII, XVIII, XIX and XX——XV (208 mg) was dissolved in 1 N HCl–MeOH (3 ml) and refluxed for 5 hr. After neutralization with Ag_2CO_3, the precipitates were filtered off. The filtrate was concentrated *in vacuo* and the residue was chromatographed on silica gel (hexane–AcOEt (5 : 1)) to give two fractions (Fr. 1, 61 mg; Fr. 2, 30 mg). Further elution with AcOEt gave a mixture of methylated sugars, which was examined by GLC. The results are summarized in Table IV. Fr. 2 (XIX) showed a single spot on TLC, but could not be crystallized. The PMR spectrum showed signals of a hydroxymethine group at δ 3.74 (C_3-H, br. s), four OCH_3 groups (3.27, 3.42, 3.49 and 3.58 ppm) and two methyl groups at C-25 at 1.30 ppm (6H, s).

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20) G. Germain, P. Main and M.M. Woolfson, *Acta crystallogr.*, **A27**, 368 (1971).

21) T. Sakurai, H. Iwasaki, Y. Watanabe, K. Kobayashi, Y. Bando and Y. Nakamichi, *Rikagaku Kenkyusho Hookoku*, **50**, 75 (1974).

Table IV. GLC (t_R in min) of Methylated Sugars in the Methanolysates of XV and XXIIa

Temperature	172°	155°	180°
Methanolysate of			
XV	3.2, 7.0		
XXIIa		1.9, 2.3 3.6, 4.9	4.7*, 5.7
References: Methyl pyranosides of			
2,3,4-tri-O-Me-α-D-xylose		2.3	
2,3,4-tri-O-Me-β-D-xylose		1.9	
2,3,4,6-tetra-O-Me-α-D-glucose	3.2	4.9	
2,3,4,6-tetra-O-Me-β-D-glucose		3.6	
2,3,4-tri-O-Me-α-D-glucose	7.0		1.9
2,3,6-tri-O-Me-α-D-glucose	6.7		1.7
2,4,6-tri-O-Me-α-D-glucose	8.7		2.2
3,4,6-tri-O-Me-α-D-glucose	6.0		1.5
2,3-di-O-Me-α-D-glucose			5.7
2,4-di-O-Me-α-D-glucose			3.6
2,6-di-O-Me-α-D-glucose			6.3
3,4-di-O-Me-α-D-glucose			3.6
3,6-di-O-Me-α-D-glucose			4.0
4,6-di-O-Me-α-D-glucose			4.1

Conditions: 5% 1,4-butanediol succinate on Shimalite W (60—80 mesh), 2.1 m × 3 mmϕ. N_2 carrier gas at 1 kg/cm^2.
* This peak may correspond to the β-anomer.

XVI (171 mg) was methanolyzed and worked up in the manner described above to give two fractions (Fr. 1′, 22 mg; Fr. 2′, 38 mg) and a mixture of methylated sugars, which gave a GLC chromatogram identical with that of the methylated sugars from XV. Fr. 2′ was crystallized from MeOH to give colorless needles (XX) (15 mg): mp 164—166°. The PMR spectrum exhibited signals of three OCH_3 groups (3.42, 3.58 and 3.64 ppm) and a $HO-\underset{|}{C}(C\underline{H}_3)_2$ group at 1.49 ppm (6H, s). Fr. 1′ showed the same IR spectrum as Fr. 1, and both fractions were combined and chromatographed on silica gel, using 10% AcOEt–hexane as an eluent, to give two thin-layer-chromatographically homogeneous compounds, XVII (28 mg) and XVIII (22.7 mg). XVII was crystallized from MeOH to provide colorless prisms, mp 198—200°. PMR: 1.84 (3H, s, $C\underline{H}_3-\overset{|}{C}=CH_2$), 3.26, 3.43, 3.47 (3H each, s, $-OCH_3$), 5.17 (2H, perturbed d, $CH_3-\overset{|}{C}=C\underline{H}_2$). CMR: olefinic carbons: 143.56(s), 143.31(s), 119.29(d), 116.08(t); oxygen-bearing carbons: 84.41(d), 81.28(d), 80.80(d), 75.97(d), 58.57(q), 57.70(q), 55.70(q); quaternary carbons: 49.17, 47.07, 41.62, 34.84. XVIII was crystallized from MeOH to give colorless needles, mp 190—193.5°. PMR: 3.44, 3.58 (3H each, s, $-OCH_3$). CMR: olefinic carbons: 143.31(s), 119.39(d); oxygen-bearing carbons: 90.64(d), 81.72(d), 81.38(d), 79.48(s), 76.02(d), 59.94(q), 59.11(q); quaternary carbons: 48.93, 47.41, 41.71, 34.89. EI-MS *m/z*: 502 (M^+), 487 (M^+-CH_3), 350 (M^+-152), 152, 134.

Acetylation of II——A solution of II (19 mg) in Ac_2O–pyridine (1 : 1) (0.5 ml) was heated on a boiling water bath for 25 hr. The reaction mixture was poured into ice-water, then the precipitates were collected by filtration, dried, and recrystallized from EtOH to give colorless fine needles (XXI), mp 133—140°. EI-MS *m/z*: 331, 271 (331-AcOH), 259, 199 (259-AcOH), 582, 508, 448, 134.

Methylation of II——II (320 mg) was methylated in the manner described for the methylation of I to give two methylates XXIIa (94 mg), colorless needles (MeOH), mp 178—180° and XXIIb (67 mg), colorless needles (MeOH), mp 167—168.5°. They exhibited PMR spectra similar (differing only in the number of methoxyl signals) to those of XV and XVI, respectively.

Methanolysis of XXIIa, Identification of Methylated Sugars——A solution of XXIIa (3 mg) in 1 N HCl–MeOH (0.1 ml) was refluxed for 1 hr. The reaction mixture was worked up as usual. The aglycone was identified as a mixture of XVII, XVIII and XIX (TLC). The methylated sugars obtained were examined by GLC, and the results are shown in Table IV.

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