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Steroid Saponins and Sapogenins of Underground Parts of *Trillium kamtschaticum* Pall. III.[1] On the Structure of a Novel Type of Steroid Glycoside, Trillenoside A,[2] an 18-Norspirostanol Oligoside

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A glycoside, mp 209—220° (decomp), $[\alpha]_D$ −142°, $C_{47}H_{70}O_{24}$, named trillenoside A (I), was isolated from the rhizomes of *Trillium kamtschaticum* Pall (Liliaceae).

The structure of its aglycone (designated trillenogenin, II), mp 250—251°, $[\alpha]_D$ −198°, $C_{26}H_{36}O_8$, was determined by X-ray crystallographic analysis of the tetraacetyl monobrosyl derivative, mp 242—244° (dec.), $[\alpha]_D$ −112°, $C_{40}H_{47}BrO_{14}S$, and I was characterized as 15-oxo-18-nor-25 R-spirosta-5,13-diene-1β,3β,21,23α,24β-pentaol 1-O-β-D-apiofuranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside. I is thus a novel type of steroid glycoside, noteworthy in that the aglycone is an 18-norspirostane derivative having an enone system in the D-ring and hydroxyl groups at C_{21} and in the F-ring, and also in that the sugar moiety is a branched-chain tetrasaccharide containing apiose.

Keywords——trillenoside A; 15-oxo-18-nor-spirostadiene-pentaol tetraglycoside; *Trillium kamtschaticum* Pall; structure determination; trillenogenin; X-ray analysis

In the preceding communication,[4] we reported the isolation of a new steroid saponin, named trillenoside A (I), as one of the major saponins from the underground parts of *Trillium kamtschaticum* Pall. Trillenoside A (I) is a novel steroid saponin in that it is the first 18-norspirostanol derivative isolated as a naturally occurring sapogenin and it is a steroid glycoside including apiose[5] in its sugar moiety. This report provides a full account of the structure determination of trillenoside A (I) based on the results of X-ray crystallographic analysis and chemical investigations.

Trillenoside A (I), obtained as a white powder (0.19% yield), mp 209—220° (dec.), $[\alpha]_D$ −142°, shows infrared (IR) absorption bands due to a hydroxyl (3700—3200 cm^{-1}) and an unsaturated carbonyl group (1690, 1625 cm^{-1}). The presence of the latter function is also suggested by the absorption maximum at 249 nm (ε=8600) in its ultraviolet (UV) spectrum. The proton magnetic resonance (PMR) spectrum shows signals due to two secondary (sec.) methyls (δ 0.94 and 1.30, 3H each, both doublets with J=6 Hz) and one tertiary (tert.) methyl (δ 1.10, 3H, singlet). Field desorption mass (FD-MS) spectrometry[6-8] [$(M+Na)^+$ ion; m/z 1041] and elementary analysis of I indicated the molecular formula $C_{47}H_{70}O_{24}$. Besides the $(M+Na)^+$ ion seen in the FD-MS spectrum, there were peaks at m/z 909 $[(M+Na)-132]^+$, 777 $[(M+Na)-2\times132]^+$ and 763 $[(M+Na)-278]^+$, which are ascribable to fragments due to

1) Part II: T. Nohara, K. Miyahara, and T. Kawasaki, *Chem. Pharm. Bull.*, **23**, 872 (1975).
2) Trillenoside A in this text corresponds to trillenoside in the foregoing communication.[4]
3) Location: *Maedashi 3-1-1, Higashi-ku, Fukuoka, 812 Japan.*
4) T. Nohara, A. Nakano, K. Miyahara, T. Komori, and T. Kawasaki, *Tetrahedron Lett.*, **1975**, 4381.
5) J. Stanek, M. Cevny, J. Kocourek, and J. Pacak, "The Monosaccharides," Academic Press, New York and London, 1963, p. 83.
6) H.-R. Schulten, T. Komori, and T. Kawasaki, *Tetrahedron*, **33**, 2595 (1977).
7) H.-R. Schulten, T. Komori, T. Nohara, R. Higuchi, and T. Kawasaki, *Tetrahedron*, **34**, 1003 (1978).
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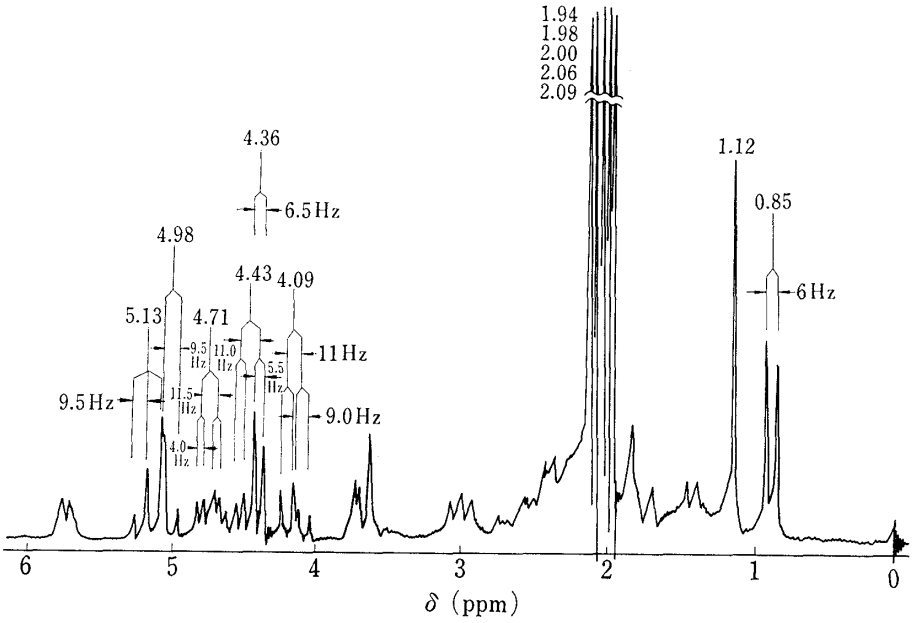

Fig. 1. PMR Spectrum of Trillenogenin Pentaacetate (III)

loss of the terminal pentose, two pentose, and pentosyl methylpentose residues, respectively. The above data indicate that I is a novel steroid tetraglycoside having three pentose and one methylpentose units.

On acid hydrolysis with 1 N H_2SO_4 in 50% ethanol, I liberated an aglycone, named trillenogenin (II), mp 250—251°, $[\alpha]_D$ −198°, together with arabinose, xylose, rhamnose and apiose as carbohydrate components. The electron impact mass spectrum (EI-MS; $M^{+\cdot}=m/z$ 476) and elementary analysis indicated II to have the formula $C_{26}H_{36}O_8$. The IR and UV spectra of II showed patterns similar to those of I, and the circular dichroism (CD) spectrum had a positive Cotton peak at 326 nm due to n-π^* transition of an enone system. Its PMR spectrum showed signals due to one sec. methyl (δ 1.01, 3H, doublet, $J=6$ Hz) and one tert. methyl (δ 1.08, 3H, singlet), as in I. II was acetylated with Ac_2O-pyridine in the usual manner to yield a pentaacetate (III), mp 243—245°, $[\alpha]_D$ −142°. Its PMR spectrum (Fig. 1) showed the signals of one sec. methyl (δ 0.85), one tert. methyl (δ 1.12) and five acetoxyl groups (δ 1.94, 1.98, 2.00, 2.06 and 2.09). In addition, signals due to the protons adjacent to the acetoxyl

Table I. CMR Data for Trillenogenin (II)

δ (ppm)	Multiplicity	Assignment	δ (ppm)	Multiplicity	Assignment
12.9	q	$-CH_3$	61.5	t	$-CH_2-O-$
13.2	q	$-CH_3$	65.0	t	$-CH_2-O-$
19.0	d	$-CH<$	68.1	d	$>CH-O-$
24.6	t	$-CH_2-$	74.2	d	$>CH-O-$
28.3	t	$-CH_2-$	75.2	d	$>CH-O-$
29.8	t	$-CH_2-$	78.4	d	$>CH-O-$
31.6	d	$-CH<$	81.4	d	$>CH-O-$
38.8	d	$-CH<$	114.4	s	$>C<^{O-}_{O-}$
42.8	t	$-CH_2-$			
43.3	s	$>C<$	124.6	d	H–C=
48.8	d	$-CH<$	138.8	s	$>C=$
49.3	d	$-CH<$	140.0	s	$>C=$
57.3	t	$-CH_2-$	175.7	s	$>C=$
			204.3	s	$>C=O$

TABLE II. Final Positional and Anisotropic Thermal Parameters with Their Standard Deviations ($\times 10^4$)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C (1)	1678(7)	638(12)	7908(32)	2(5)	22(10)	292(64)	26(11)	8(30)	−16(49)
C (2)	1382(9)	−57(12)	8225(30)	23(6)	7(10)	189(55)	5(13)	−8(33)	69(42)
C (3)	1835(9)	−613(12)	8306(33)	21(6)	11(10)	289(69)	−27(13)	−1(36)	120(48)
C (4)	2215(10)	−448(14)	9578(28)	23(6)	30(12)	137(49)	−33(15)	−16(31)	26(43)
C (5)	2472(10)	216(13)	9199(26)	17(5)	33(13)	85(44)	9(14)	−6(28)	13(41)
C (6)	2977(8)	282(13)	9098(27)	12(5)	25(11)	133(47)	−9(12)	−37(29)	2(42)
C (7)	3287(8)	909(11)	8877(29)	14(5)	7(10)	184(49)	22(11)	31(29)	21(40)
C (8)	2936(10)	1552(13)	9245(27)	24(7)	28(12)	110(47)	−28(14)	33(30)	13(41)
C (9)	2380(9)	1506(12)	9482(28)	13(5)	21(10)	159(51)	27(12)	−35(29)	−39(40)
C (10)	2075(8)	865(12)	9099(26)	12(5)	23(11)	106(43)	−2(12)	−14(26)	9(39)
C (11)	2084(9)	2256(15)	8528(31)	15(5)	50(14)	198(59)	−10(15)	13(31)	128(53)
C (12)	2373(8)	2830(13)	7633(29)	8(5)	39(12)	204(57)	19(14)	−63(29)	61(47)
C (13)	2973(9)	2808(15)	8031(29)	19(6)	55(14)	114(49)	0(16)	27(30)	−79(49)
C (14)	3194(8)	2236(15)	8841(28)	8(5)	65(14)	122(46)	51(14)	−36(27)	−55(48)
C (15)	3756(9)	2476(12)	9041(28)	21(6)	14(11)	143(50)	9(12)	−30(30)	39(42)
C (16)	3906(9)	3127(13)	8036(29)	19(6)	35(12)	124(48)	3(14)	9(30)	45(46)
C (17)	3360(8)	3451(13)	7588(27)	8(5)	37(12)	123(47)	0(12)	−1(26)	−14(43)
C (19)	1833(10)	1021(14)	10640(29)	21(6)	41(13)	149(56)	−4(15)	34(32)	28(47)
C (20)	3334(8)	4145(12)	8491(25)	10(5)	26(11)	87(44)	11(12)	−19(25)	31(37)
C (21)	2991(9)	4678(13)	7650(29)	22(6)	25(11)	140(52)	2(14)	−3(31)	−84(44)
C (22)	3916(8)	4388(13)	8605(24)	13(5)	33(11)	32(37)	3(12)	−19(24)	−8(34)
C (23)	4077(9)	4917(13)	9733(26)	21(6)	28(12)	63(41)	−6(15)	−4(28)	46(39)
C (24)	4688(9)	5070(13)	9710(28)	11(5)	32(12)	192(51)	1(14)	−16(31)	−30(43)
C (25)	4849(10)	5332(15)	8113(27)	26(7)	59(14)	88(47)	−27(17)	−32(32)	75(48)
C (26)	4684(9)	4739(14)	7076(30)	11(5)	55(12)	183(53)	−22(15)	11(33)	−57(51)
C (27)	5493(9)	5371(16)	7962(31)	12(6)	94(18)	171(54)	−62(17)	−1(31)	96(59)
C (28)	1024(10)	1282(14)	6734(33)	22(6)	28(12)	285(67)	12(14)	99(37)	11(51)
C (29)	520(11)	1792(15)	6805(32)	37(8)	46(15)	186(61)	37(18)	−15(39)	85(53)
C (30)	1700(10)	−1838(17)	8459(31)	24(7)	78(18)	118(55)	−29(18)	−3(34)	103(54)
C (31)	1323(10)	−2530(14)	8688(33)	31(7)	31(13)	207(61)	17(16)	10(38)	56(52)
C (32)	3212(8)	6511(12)	7576(26)	11(5)	23(10)	89(44)	5(12)	1(25)	−12(38)
C (33)	3418(11)	7065(19)	8517(33)	29(7)	119(23)	161(62)	−76(22)	24(38)	3(69)
C (34)	3883(12)	7452(19)	8118(36)	34(8)	101(21)	205(67)	−44(22)	37(41)	−98(20)
C (35)	4086(9)	7256(10)	6742(33)	6(5)	62(15)	272(65)	3(15)	7(32)	−16(60)
C (36)	3876(10)	6792(13)	5664(34)	29(7)	15(11)	280(71)	5(15)	43(29)	48(50)
C (37)	3414(9)	6417(14)	6111(31)	21(6)	38(13)	157(52)	−3(14)	10(34)	55(49)
C (38)	3765(10)	5068(14)	12309(31)	25(7)	32(13)	199(56)	2(16)	−18(34)	−78(49)
C (39)	3710(11)	4715(16)	13805(29)	41(8)	61(16)	50(44)	−23(19)	92(36)	−54(51)
C (40)	5020(10)	5503(14)	12169(31)	19(6)	43(12)	178(56)	5(15)	−38(33)	−12(49)
C (41)	5123(11)	6193(14)	12926(33)	33(8)	41(13)	206(63)	−3(17)	−53(39)	−86(53)
O (1)	1258(6)	1182(9)	7921(19)	27(4)	35(8)	115(32)	8(10)	−39(20)	8(29)
O (3)	1487(6)	−1226(9)	8708(22)	24(4)	35(8)	248(41)	18(9)	3(25)	19(34)
O (15)	4067(6)	2206(10)	9944(21)	16(4)	43(9)	234(38)	2(16)	−24(20)	59(34)
O (16)	4176(6)	3716(9)	8910(18)	13(3)	41(8)	100(28)	−9(9)	−4(18)	0(28)
O (21)	2896(6)	5291(9)	8704(18)	23(4)	35(8)	111(29)	15(9)	27(20)	19(28)
O (22)	4090(6)	4622(9)	7169(18)	21(4)	41(8)	105(30)	−13(9)	−13(20)	9(29)
O (23)	3952(6)	4647(8)	11170(19)	14(3)	24(7)	162(31)	−15(8)	10(20)	11(29)
O (24)	4808(6)	5648(9)	10717(20)	10(3)	35(8)	252(40)	−1(9)	−18(21)	17(31)
O (28)	1126(9)	1024(12)	5417(26)	46(7)	69(12)	333(57)	13(16)	−42(33)	88(48)
O (30)	2164(7)	−1971(9)	8009(23)	35(5)	28(8)	271(44)	12(10)	32(27)	47(35)
O (38)	3610(8)	5658(10)	12076(22)	40(6)	50(10)	186(38)	16(13)	42(28)	−4(36)
O (40)	5064(7)	4921(9)	12552(22)	28(4)	44(8)	198(36)	−2(11)	−70(21)	−3(33)
OSA	2414(6)	6357(9)	9355(9)	20(4)	40(8)	167(5)	11(10)	27(20)	21(30)
OSB	2327(6)	5879(8)	6915(19)	20(4)	30(7)	174(33)	8(19)	−50(21)	−7(30)
S	2644(3)	6020(4)	8118(8)	15(1)	33(3)	116(12)	10(4)	−9(8)	−16(12)
Br	4713(1)	7774(3)	6178(5)	23(1)	108(3)	356(9)	−43(3)	10(5)	77(9)

Anisotropic thermal parameters are in the form $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$

functions appeared at δ 4.09, 4.43, 4.71, 4.98, 5.13 and around 4.60 (multiplet) (one proton each). A signal at δ 4.36 may be that of one proton next to the ether oxygen because it was not shifted towards higher field by permethylation. Since there are six protons geminal to five acetoxyl functions in III, two of them are regarded as bound to the carbon bearing the primary alcohol group in II. Taking into account their coupling constants, it is suggested that the protons at δ 4.98 (1H, doublet, J=9.5 Hz) and δ 5.13 (1H, triplet, J=9.5 Hz) are vicinal and those at δ 4.09 (1H, quartet, J=9, 11 Hz) and δ 4.43 (1H, quartet, J=5.5, 11Hz) are geminal, namely forming a hydroxymethylene moiety. In addition, one proton signal at δ 5.58 and two protons around δ 3.50—3.70 are assignable respectively to an olefinic proton and protons attached to a carbon bearing ether oxygen. In carbon-13 nuclear magnetic resonance spec-

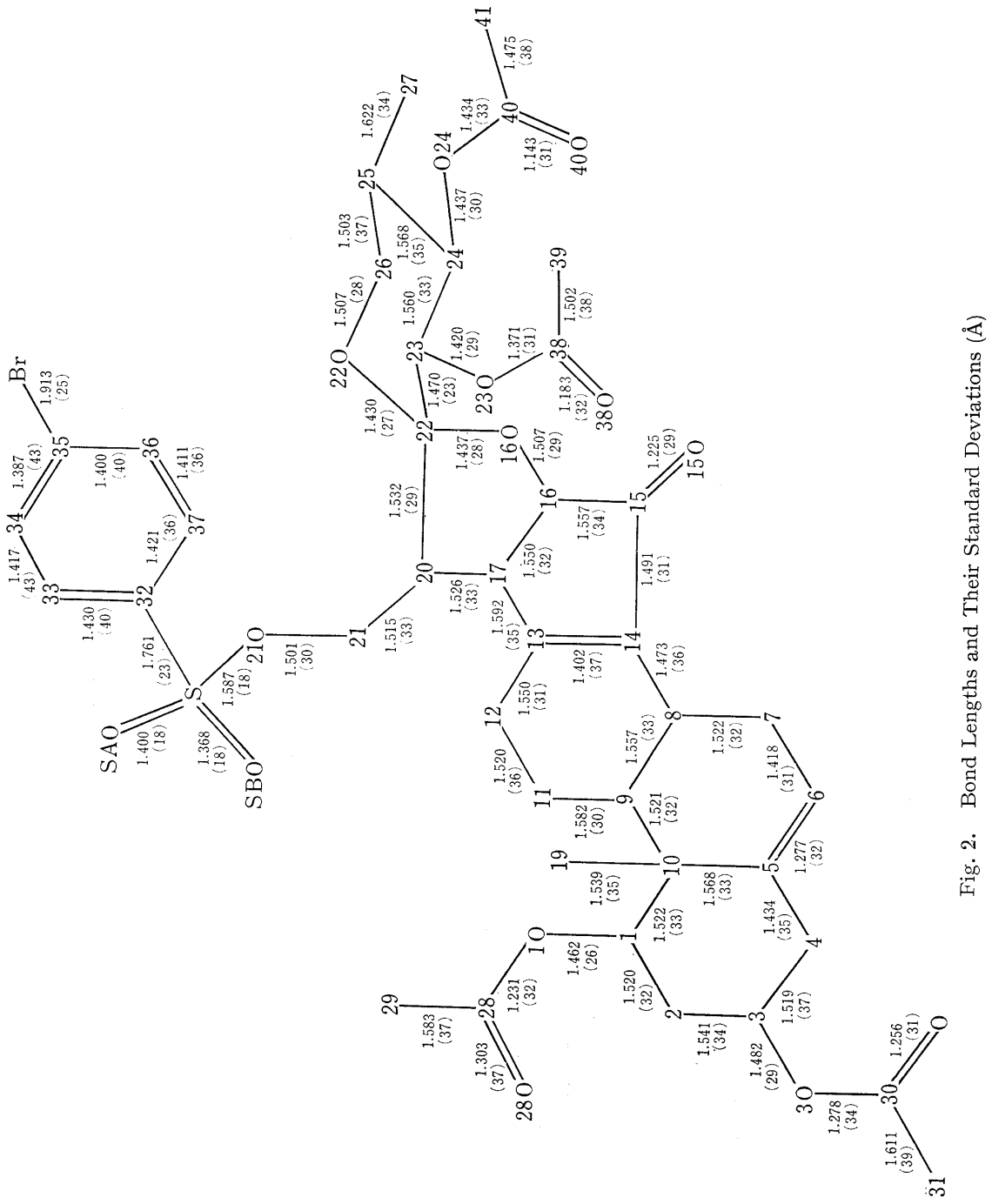

Fig. 2. Bond Lengths and Their Standard Deviations (Å)
The standard deviation for the last digit is given in parentheses.

trometric (CMR) studies of II using the off-resonance decoupling technique, one tetra-substituted double bond (δ 175.7 and 138.8 ppm), one tri-substituted double bond (δ 140.0 and 124.6 ppm), one carbonyl (δ 204.3 ppm) and eight carbons bearing oxygen functions were detected (Table I).

Based on the above results, it is conceivable that four of the eight oxygen atoms in II correspond to sec. hydroxyl, two are ether oxygens and the other two exist as a ketone and a primary hydroxyl group. The degree of unsaturation of II can be accounted for by one ketone, two double bonds and six rings.

The complexity of a molecule containing twenty-six carbons and eight oxygenated functions prompted us to attempt X-ray crystallography.

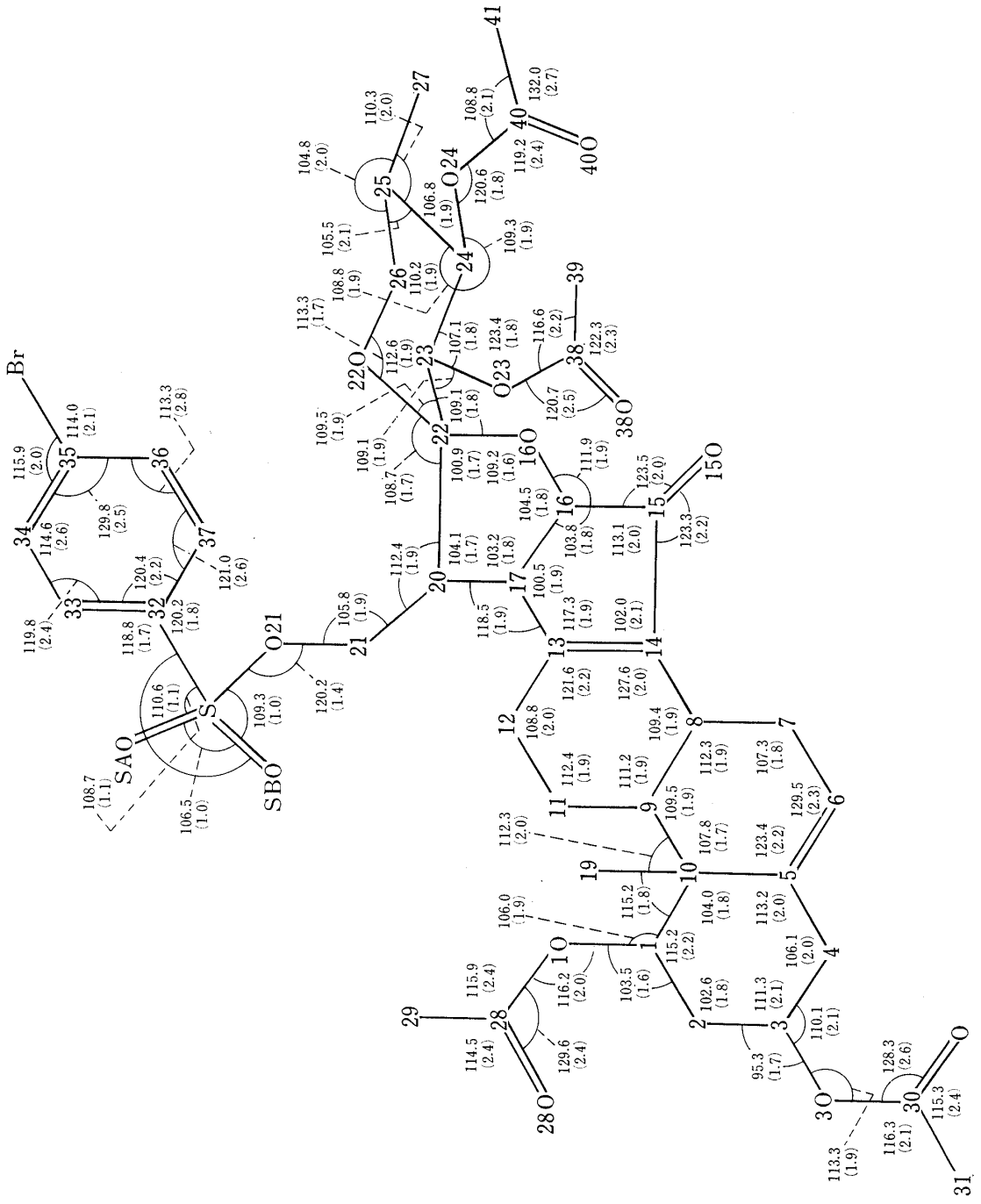

Fig. 3. Bond Angles and Their Standard Deviations (°)
The standard deviation for the last digit is given in parentheses.

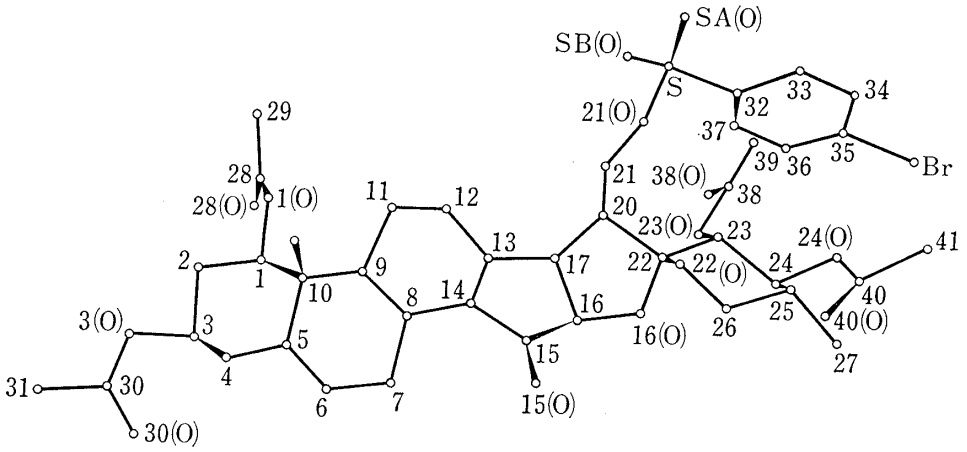

Fig. 4. ORTEP Drawing of Tetraacetyl Trillenogenin Monobrosylate (IV)
Perspective view along the crystal c axis; −10° rotation around the b axis.

For this purpose, a bromine derivative of II, tetraacetyl monobrosylate (IV), mp 242—244°, was used. The structure was solved by the heavy atom method.[9] The coordinates of the bromine atom were obtained from the three-dimensional Patterson synthesis. By putting those of the bromine atom into the Fourier calculation, the sulfur atom was located. All 56 nonhydrogen atoms appeared successively during 6 cycles of Fourier synthesis (R=0.295). Subsequent block-diagonal least-squares refinement using 1748 observed reflections with isotropic and then anisotropic thermal factors gave the detailed molecular structure and reduced the final R factor value to 0.092. The positional and thermal parameters with their standard deviations are listed in Table II. The bond lengths and bond angles are given in Fig. 2 and 3, respectively. An ORTEP drawing[10] of the molecular structure (or its mirror image) of IV is presented in Fig. 4. Since the n-π^* transition due to the enone system shows a positive Cotton effect curve, as mentioned before, the absolute configuration of II was deduced to be normal steroid form based on the Snatzke rule[11] for transoid cyclopentenones.

Consequently II is 15-oxo-18-nor-25R-spirosta-5,13-diene-1β,3β,21,23α,24β-pentaol.[12] This is the first reported natural occurrence of an 18-norspirostane derivative, and II possesses the following additional structural peculiarities: 1) an enone system in the D-ring, 2) a hydroxylated 21-methyl group, 3) a glycol structure of the F-ring.

As with II, the IR, UV and CD spectra of I indicate the presence of an enone system and the PMR spectrum shows *tert.* and *sec.* methyls; thus, II is unlikely to be an artefact produced secondarily during the hydrolysis of I, and should be the genuine aglycone of I.

Next, the sugar moiety of I was investigated as follows (Chart 1).

The permethylate (V), $[\alpha]_D$ −102°, which was derived from I by the Kuhn method,[13] on methanolysis gave an aglycone derivative (VI), $[\alpha]_D$ −201°, and a mixture of methylated sugars. The latter was shown to be the mixture of methyl 2,3,5-tri-O-methyl-apiofuranoside,[14] methyl 2,3,4-tri-O-methyl-xylopyranoside, methyl 2,4-di-O-methyl-rhamnopyranoside and methyl 4-O-methyl-arabinopyranoside by means of gas liquid chromatography (GLC) and thin layer chromatography (TLC). In particular, apiofuranoside[13] isolated from the mixture

9) T. Komori, T. Kawasaki, K. Kamiya, and Y. Wada, *Chem. Pharm. Bull.*, **25**, 1701 (1977).
10) C.K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1965.
11) G. Snatzke, *Tetrahedron*, **21**, 421 (1965).
12) The absolute configuration at C_{25} of II having the 24-hydroxyl group is S, but the nucleus is the 25R-spirostane.
13) R. Kuhn, I. Löw, and H. Trischmann, *Chem. Ber.*, **88**, 1492, 1690 (1955).
14) *a*) D.H. Ball, F.H. Bisset, J.L. Klundt, and L. Long, *Carbohyd. Res.*, **17**, 165 (1971); *b*) I. Kitagawa, A. Inaba, and I. Yoshioka, *Chem. Pharm. Bull.*, **23**, 2268 (1975); *c*) A. Tada, T. Kaneiwa, J. Shoji, and S. Shibata, *Chem. Pharm. Bull.*, **23**, 2965 (1975).

of methylated sugars was identical with that derived from apiin[5] permethylate (TLC, GLC, $[\alpha]_D$ and PMR).

The above methylated sugars were hydrolyzed and separated to yield 2,3,5-tri-O-methyl-D-apiofuranose, 2,3,4-tri-O-methyl-D-xylopyranose, 2,4-di-O-methyl-L-rhamnopyranose and 4-O-methyl-L-arabinopyranose. On the basis of the FD–MS spectrum of I and the EI–MS spectrum of V [m/z 1200; $M^{+}\cdot$, m/z 349; $C_{16}H_{29}O_8$ (penta-O-methyldisaccharidyl cation) and m/z 175; $C_8H_{15}O_4$ (terminal tri-O-methyl pentosyl cation)]. It is evident that I consists of one mol each of II, D-apiose, D-xylose, L-arabinose and L-rhamnose. Both D-apiose and D-xylose are located at the terminals of a tetrasaccharide branched at arabinose.

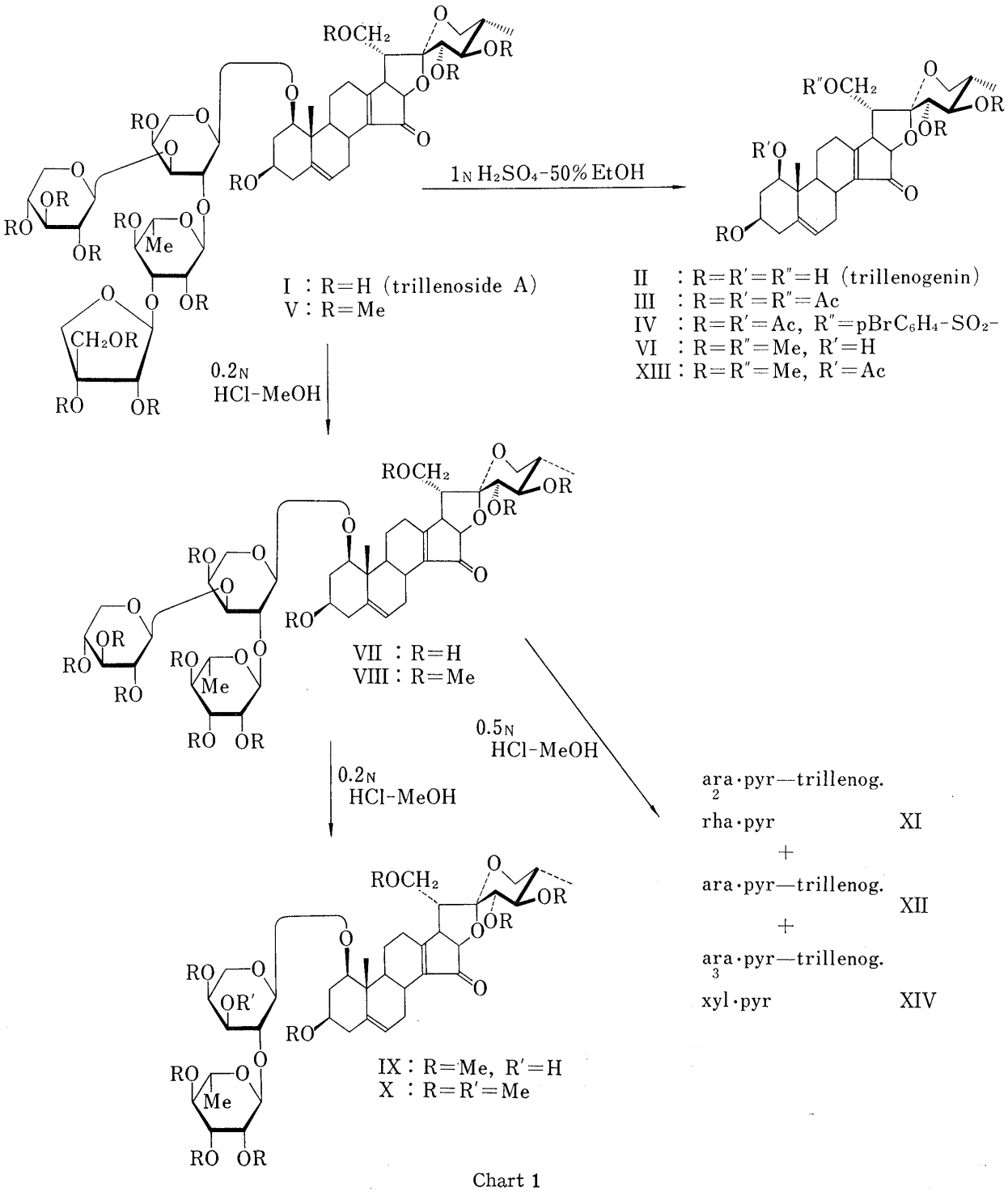

Chart 1

D-xyl·pyr——^{3}L-ara·pyr——
^{2}|
D-api·fur ——^{3}L-rha·pyr

Fig. 5

Partial hydrolysis of I with 0.2 N HCl–MeOH gave a prosapogenin (VII), $[\alpha]_D$ −112°, whose permethylate (VIII), $[\alpha]_D$ −100°, on methanolysis yielded methyl 2,3,4-tri-O-methyl-rhamnopyranoside, methyl 2,3,4-tri-O-methyl-xylopyranoside and methyl 4-O-methyl-arabinopyranoside. Further partial hydrolysis of VIII gave (IX), $[\alpha]_D$ −98°, and the methanolysis of its permethylate (X) yielded methyl 2,3,4-tri-O-methyl-rhamnopyranoside and methyl 3,4-di-O-methyl-arabinopyranoside. Consequently the sequence of sugar moiety is as shown in Fig. 5. The anomeric configuration of each monosaccharide was determined from the molecular rotation differences[15] (see Table III) between V, VIII, VII, II-rhamnosyl arabinoside (XI), $[\alpha]_D$ −118°, and II-arabinoside (XII), $[\alpha]_D$ −142°, mp 223—226°, the latter two of which were derived from VII by partial hydrolysis with 0.5 N HCl in MeOH. The linkages of D-apiose, D-xylose, L-arabinose and L-rhamnose units are β, β, α and α, respectively. These results are consistent with the chemical shifts and coupling constants of anomeric protons in the PMR spectrum of I (see "Experimental").

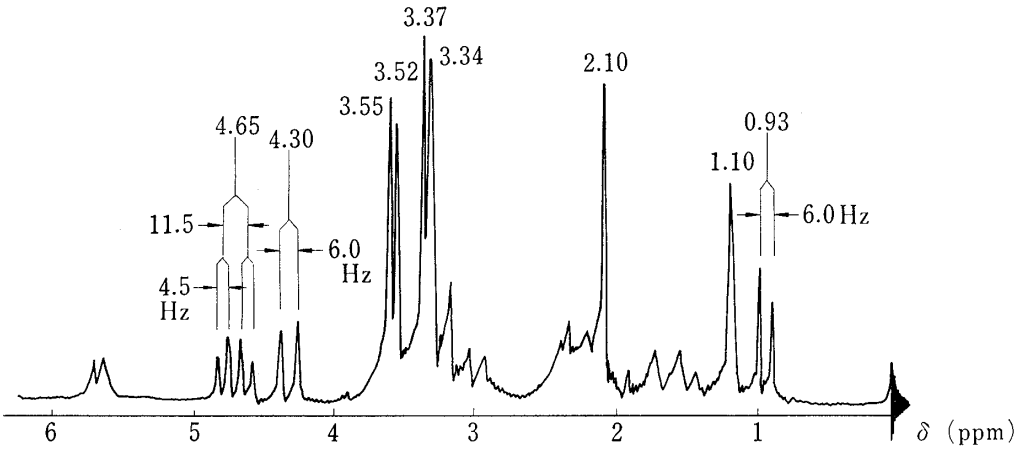

Fig. 6. PMR Spectrum of Monoacetyl Trillenogenin Tetramethylether (XIII)

Table III. Molecular Rotation Differences of V—VIII, VII—XI, XI—XII and XII—II

II—Ara^{2}—Rha^{3}—Api ^{3}| Xyl (Me)	V	−1224°	−184°	Me 2,3,5-tri-O-Me-α-D-api·furanoside β-anomer	+239°[14] −163°
II—Ara^{2}—Rha ^{3}| Xyl (Me)	VIII	−1040°			
II—Ara^{2}—Rha ^{3}| Xyl	VII	−992°	−120°	Me β-D-xyl·pyranoside α-anomer	−107°[16a] +249°
II—Ara—Rha	XI	−890°	−24°	Me α-L-rha·pyranoside β-anomer	−111°[16a] +170°
II—Ara	XII	−866°	+76°	Me α-L-ara·pyranoside β-anomer	+29°[16b] +403°
Trillenogenin	II	−942°			

15) W. Klyne, *Biochem. J.*, **47**, xli (1950).
16) *a*) M. Kimura, M. Tohma, and I. Yoshizawa, *Chem. Pharm. Bull.*, **16**, 1228 (1968); *b*) M. Kimura, M. Tohma, I. Yoshizawa, and H. Akiyama, *ibid.*, **16**, 25 (1968).

In order to determine the site of linkage of the branched sugar to the aglycone the PMR spectrum of III was compared with that of VI acetate (XIII), mp 171—174°, $[\alpha]_D$ −210°. In Fig. 1, the protons (C_3–H, C_{24}–H, C_{23}–H and C_{21}–H_2) of carbons bearing an acetoxyl group were observed at around δ 4.60, 5.13, 4.98, 4.43 and 4.09, respectively. In the PMR spectrum of XIII (Fig. 6), four methoxyl and one acetoxyl groups were apparent [δ 3.34, 3.37, 3.52 and 3.55 (3H each, singlet, OMe×4) and 2.10 (3H, singlet OAC×1)]. Since the quartet signal at δ 4.65 (1H, J=4.5, 11.5 Hz), which is assigned to the one proton geminal to acetoxyl, corresponds to that at δ 4.71 (1H, quartet, J=4.0, 11.5 Hz) ascribable to C_1–H in the spectrum of III, it is evident that C_1–OH is acetylated, that is, the sugar chain is linked to C_1–OH.

Furthermore, as I possesses no sugar component other than the branched four-monosaccharide moiety, the possibility that I could be the 3,26-O-bisglycoside corresponding to II can be ruled out. Consequently, I is defined as trillenogenin 1-O-β-D-apiofuranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Glycosides of flavones,[5] isoflavones,[17] anthraquinones[18] and triterpenes[14b,c] with apiose in the sugar moiety have been identified, but I is the first such example of a steroid glycoside.

Experimental

Melting points were determined on a Kofler block and are uncorrected. Optical rotations were taken with a JASCO DIP-SL automatic polarimeter at 23—28°. CD spectra were measured using a JASCO ORD/UV-5 recording spectropolarimeter. IR spectra were obtained with a JASCO IR-G spectrometer. CMR data were taken in C_5D_5N solution (0.6 M) on a JEOL-FX-100 spectrometer (25.05 MHz) under the following conditions: temperature 30°, pulse width 5 μs (45°), repetition time 1 sec, accumulation time 0.3399 sec, data points 8192. PMR spectra were recorded at 100 MHz on a JEOL PS-100 spectrometer; in the CMR and PMR studies, a 5 mm ϕ sample tube was used. Chemical shifts are expressed in ppm from tetramethylsilane as an internal reference, and coupling constants (J) are given in Hz. Abbreviations used are: s=singlet, d=doublet, t=triplet, q=quartet. FD-MS spectra were recorded on a JEOL D-300 instrument (equipped with an FD/FI/EI ion source) at an ion source pressure of 3×10^{-7} Torr and an ion source temp. between 60° and 70°. Ion source potentials were +2.5 kV for the field anode and −5 kV for the slotted cathode plate. EI-MS spectra were measured on a JEOL JMS-01SG double focusing mass spectrometer with direct insertion of the probe into the ion source. In measurements of high resolution spectra using the photo plate method, Ilford type Q_2 thin glass was used as a dry plate and perfluorokerosene was employed as an internal calibration standard. The average accuracy in the mass determination was ±3 mmu. Spectra were recorded with an accelerating potential of 5.0—6.0 kV, an ionizing potential of 30—75 eV and a sample temperature of 150—200°. TLC and column chromatographies were carried out on Kiesel gel G nach Stahl (Merck) and with Kieselgel (0.05—0.2 mm), respectively. The solvents used were as follows: a, lower phase of $CHCl_3$–MeOH–H_2O=65: 35: 10; b, benzene–acetone=1: 1; c, benzene–acetone=3: 1; d, hexane–AcOEt=1: 1. GLC was run on a JEOL JGC 1100 machine with a flame ionization detector using a glass column (3 mm×2 m) packed with 1.5% 1,4 butanediol succinate polyester on Shimalite. Paper partition chromatography (PPC) for sugars was conducted on Toyo Roshi No. 50 paper using the upper layer of n-BuOH–AcOH–H_2O (4: 1: 5) as a solvent and aniline hydrogen phthalate as a staining agent.

Trillenoside A (I)——Further purification by silica gel chromatography (solv., CH_2Cl_2–MeOH–water=7: 3: 0.4) of the compound Ty (24.5 g) in Chart 2 in the preceding paper[1] afforded two homogeneous compounds, Ty-1 and the less polar Ty-2.[19] Ty-1 was designated as trillenoside A and crystallized from MeOH–acetone to give a white powder (20.5 g, 0.19%), mp 209—220° (dec.), Rf 0.16 (solv. a), $[\alpha]_D$ −116.4° (c=1.23, MeOH). *Anal.* Calcd for $C_{47}H_{70}O_{24}\cdot 2H_2O$: C, 53.50; H, 7.02. Found: C, 53.28; H, 7.04. IR ν_{max}^{KBr} cm^{-1}: 3700—3200 (OH), 1690, 1625 (enone). UV λ_{max}^{EtOH} nm (ε): 249 (8600). CD $[\theta]_{322}$: +2990 (c=0.023, EtOH, positive max.). PMR ($CDCl_3$–CD_3OD–D_2O+CF_3COOH[20]) 0.94 (3H, d, J=6 Hz, 27-Me), 1.10 (3H, s, 19-Me), 1.30 (3H, d, J=6 Hz, rhamnosyl 6-Me), 4.32 [1H, multiplet (m), arabinosyl 1-H[21]], 4.46, 4.48 (1H each, both d of J=6.5 Hz, xylosyl 1-H and 16-H of aglycone), 5.26 (1H, d, J=3 Hz. apiosyl 1-H), 5.36 (1H, broad

17) A. Malhotra, V.V.S. Murti, and T.R. Seshadri, *Tetrahedron*, 23, 405 (1967).
18) H. Wagner and G. Demuth, *Tetrahedron Lett.*, 1972, 5013.
19) Ty-2 was named trillenoside B and crystallized from MeOH–acetone to yield a white powder (2.5 g, 0.023%), mp 235—241° (dec.). The structure will be reported in Part IV of this series.
20) K. Miyahara and T. Kawasaki, *Chem. Pharm. Bull.*, 22, 1407 (1974).
21) Assignment of the anomeric proton of the arabinosyl moiety in the foregoing report[4] should be corrected as indicated here.

s, rhamnosyl 1-H). FD-MS *m/z*: 1041 (M+Na), 909 (M+Na−132), 777 [M+Na−(133×2)], 763 [(M+Na)−278].

Acid Hydrolysis of I——I (3.1 g) was refluxed with 1 N H_2SO_4 in 50% EtOH (30 ml) on a boiling water bath for 2 hr, then the solution was diluted with water (20 ml) and concentrated to 1/2 volume. The residue was heated on a boiling water bath for a further one hr, neutralized with 3% KOH–MeOH and evaporated to dryness. The salts that deposited on addition of MeOH were filtered off and the filtrate was passed through a Sephadex LH-20 column, eluting with MeOH, to give the hydrolysate which was chromatographed on silica gel (100 g, solv., $CHCl_3$–MeOH–water=7: 3: 0.2→7: 3: 0.5) to provide the aglycone fraction (*Rf* 0.53, solv., a) and a sugar mixture.

Trillenogenin (II)——Trillenogenin (II) was recrystallized from water to give 460 mg of colorless plates; mp 250—251°, $[\alpha]_D$ −198.0° (*c*=1.05, MeOH); $[M]_D$ −194°, $[\alpha]_D$ −214.7° (*c*=0.86, pyridine). *Anal.* Calcd for $C_{26}H_{36}O_8$: C, 65.53; H, 7.62. Found: C, 65.23; H, 7.68. IR ν_{max}^{KBr} cm^{-1}: 3600—3100 (OH), 1695, 1625 (enone), 1000, 975, 930, 878, 831 (spiroketal). UV λ_{max}^{EtOH} nm (*ε*): 248.5 (12800). CD $[\theta]_{326}$: +4690 (*c*=0.018, EtOH: positive Cotton effect). EI-MS *m/z*: 476 ($M^{+\cdot}$), 375 ($C_{21}H_{27}O_6$), 388 ($C_{22}H_{28}O_6$), 301 ($C_{19}H_{25}O_3$), 284 ($C_{18}H_{20}O_3$), 147 ($C_6H_{11}O_4$). PMR (d_5-pyridine) *δ*: 1.01 (3H, d, *J*=6 Hz, *sec.*Me), 1.08 (3H, s, *tert.*Me).

Detection of Sugars——The sugar mixture was examined by PPC; it contained rhamnose (*Rf* 0.43), apiose (*Rf* 0.39), xylose (*Rf* 0.32), arabinose (*Rf* 0.30).

Trillenogenin Pentaacetate (III)——The conventional acetylation of II (70 mg) with Ac_2O–pyridine (1: 1, 5 ml each) at room temperature overnight or under reflux for 1 hr at 100° gave trillenogenin pentaacetate (III), 50 mg of colorless plates from EtOH, mp 243—245°, $[\alpha]_D$ −141.5° (*c*=1.05, $CHCl_3$). *Anal.* Calcd for $C_{36}H_{46}O_{13}$: C, 62.96; H, 6.75. Found: C, 62.67; H, 6.84. IR ν_{max}^{KBr} cm^{-1}: 1770—1748 (OAc), 1720, 1645 (enone), 1240 (OAc), 980, 925, 897, 870 (spiroketal). UV λ_{max}^{EtOH} 244.2 nm (*ε*=9200). PMR ($CDCl_3$) *δ*: 0.85 (3H, d, *J*=6 Hz, 27-Me), 1.12 (3H, s, 19 Me), 1.94, 1.98, 2.00, 2.06, 2.09 (OAc×5), 4.09 (1H, q, *J*=9.0, 11.0 Hz, 21-Ha), 4.36 (1H, d, *J*=6.5 Hz, 16-H), 4.43 (1H, q, *J*=5.5, 11.0 Hz, 21-Hb), 4.71 (1H, q, *J*=4.0, 11.5 Hz, 1-H), 4.98 (1H, d, *J*=9.5 Hz, 23-H), 5.13 (1H, t, *J*=9.5 Hz, 24-H). CD $[\theta]_{330}$: +6250 (*c*=0.032, EtOH, positive Cotton effect). EI-MS *m/z*: 686 ($M^{+\cdot}$).

Trillenogenin Tetraacetate Monobrosylate (IV)——A mixture of II (90 mg), pyridine (5 ml) and *p*-bromobenzenesulfonyl chloride (40 mg) was stirred for 3 hr at room temperature. The reaction mixture was poured into water and extracted with *n*-BuOH, then the organic layer was taken up and concentrated *in vacuo* to give the residue, which was chromatographed on a silica gel column (30 g) to give a syrup (55 mg) with an *Rf* value of 0.25 (solv.b). It was acetylated (Ac_2O–pyridine, 1: 1, 10 ml) and purified by silica gel column chromatography (20 g, solv., hexane–AcOEt 2: 1) to yield colorless plates, *Rf* 0.56 (solv. d), mp 242—244° (dec.), $[\alpha]_D$ −111.6° (*c*=1.12, $CHCl_3$). *Anal.* Calcd for $C_{40}H_{47}BrSO_{14}$: C, 55.62; H, 5.48. Found: C, 55.97; H, 5.41. IR ν_{max}^{KBr} cm^{-1}: 1770—1730 (OAc), 1710, 1632 (enonε), 1578, 820, 747 (phenyl group), 970, 877 (spiroketal). PMR ($CDCl_3$): 0.81 (3H, d, *J*=6 Hz, 27-Me), 1.12 (3H, s, 19-Me), 1.96, 2.00, 2.02, 2.10 ($OCOCH_3$×4), 7.70—7.92 (arom.protons×4), 4.18 (1H, d, *J*=7 Hz, 16-H), 4.78 (1H, d, *J*=10 Hz, 23-H), 4.60—4.68 (2H, 3- and 1-H), 5.10 (1H, t, *J*=10 Hz, 24-H), 5.70 (1H, broad d, *J*=5 Hz, 6-H), CD $[\theta]_{324}$: +4500 (*c*=0.02, EtOH).

Permethylether (V) of I——A mixture of I (1.2 g), dimethylformamide (DMF, 10 ml), CH_3I (10 ml) and silver oxide (3 g) was stirred overnight (Kuhn method). This procedure was repeated twice more. After usual work-up, a syrup was obtained and it was purified by silica gel column chromatography (50 g, solv. c) to afford a white powder (710 mg), $[\alpha]_D$ −101.9° (*c*=0.93, $CHCl_3$), *Rf* 0.37 (solv. c). *Anal.* Calcd for $C_{60}H_{96}O_{24}$: C, 59.98; H, 8.05. Found: C, 59.72; H, 8.07. UV λ_{max}^{EtOH} 247.4 nm (*ε*=7200). IR: no OH. EI/MS *m/z*: 1200 ($M^{+\cdot}$), 514 ($C_{30}H_{42}O_7$), 384 ($C_{23}H_{28}O_5$), 349 ($C_{16}H_{29}O_8$), 175 ($C_8H_{15}O_4$).

Crystallographic Analysis of IV——The cell parameters and intensities of a crystal with approximate dimensions of 0.1×0.2×0.3 mm were measured on a Syntex P1 automated diffractometer with graphite-monochromated Mo K*α* radiation (*λ*=0.71069 Å). The cell parameters were determined by the autoindexing and least-squares program for 15 reflections. The crystal data were: $C_{40}H_{47}BrO_{14}S$ (M.W.=863.758), orthorhombic, *a*=25.099 (16), *b*=18.607 (11), *c*=8.982 (5) Å, *V*=4194.6 (4.3) Å^3, *Dm*=1.386 g/cm^3 (flotation method in CCl_4-benzene solution), *Dc*=1.368 g/cm^3, *Z*=4, space group $P2_12_12_1$. Intensities were collected by the *θ*—2*θ* scan technique with a variable scan rate of 4.0 to 24.0°/min. Three standard reflections were monitored every 50 reflections and their intensities showed good stability. A total of 3184 independent reflections with 2*θ*<60° was collected. The I values of 1748 reflections greater than 2 *σ*(I) were used for the structure analysis. They were corrected for Lorenz and polarization effects, but correction for absorption was not applied. All the calculations were performed on FACOM 23060, 23075 and M-190 computers at the Computer Center of Kyushu University.

Methanolysis of V——V (420 mg) was dissolved in 1 N HCl–MeOH (15 ml), refluxed for 2 hr on a bath and neutralized with 3% KOH–MeOH. The salts that deposited were filtered off, and the filtrate was concentrated and passed through a Sephadex LH-20 column with MeOH to give the hydrolysate, which was subjected to TLC and GLC. TLC: solv. d, GLC: column temp. 180°, N_2 1.22 kg/cm^2, methyl 2,3,4-tri-O-methyl-D-xylopyranoside (*β*), *Rf* 0.06, t_R 56;" (*α*), *Rf* 0.46, t_R1′ 11″, methyl 2,3,5-tri-O-methyl-*β*-D-apiofuranoside (*β*), *Rf* 0.52, t_R1′ 11″, methyl 2,4-di-O-methyl-*α*-L-rhamnopyranoside, *Rf* 0.29, t_R 2′ 13″, methyl 4-O-methyl-L-arabinopyranoside, *Rf* 0.02 [*Rf* 0.33(*α*), 0.38 (*β*)]. t_R (*β*) 7′ 2″, (*α*) 14′ 50″. The hydrolysate

was separated into methyl apioside (55 mg), the aglycone derivative (VI, 65 mg) and the other methylated sugars by silica gel column chromatography (40 g, solv., hexane–AcOEt=1: 1→1: 2).

Methyl 2,3,5-Tri-O-methyl-β-D-apiofuranoside

a. From the Methanolysate of V——$[\alpha]_D$ −56.2° (c=0.51, $CHCl_3$), PMR ($CDCl_3$) δ: 3.40, 3.42, 3.46, 3.50 ($OCH_3\times4$), 3.92 (1H, d, J=10 Hz, 4-H), 4.09 (1H, d, J=10 Hz, 4-H'), 4.95 (1H, d, J=3 Hz, 1-H). EI-MS m/z: 206 ($M^{+\cdot}$), 175 ($C_8H_{15}O_4$), 161 ($C_7H_{13}O_4$), 143 ($C_7H_{11}O_3$), 129 ($C_6H_9O_3$), 111 ($C_6H_7O_2$), 101 ($C_5H_9O_2$), 88 ($C_4H_8O_2$), 75 ($C_3H_7O_2$), 73 ($C_3H_5O_2$), 71 (C_4H_7O).

b. From the Methanolysate of Apiin Permethylate——The fresh parsley[22] (100 g) was extracted with EtOH (700 ml) under reflux and the solvent was removed from the extract to give the residue, to which $CHCl_3$ was added. The portion (3 g) insoluble in $CHCl_3$ was chromatographed on silica gel (90 g, solv., CH_2Cl_2–MeOH–H_2O=7: 3: 0.5) to afford a pale yellow materials (mp 228—230°). This substance was hydrolyzed with 2 N HCl–MeOH (10 ml) under reflux, neutralized and passed through Sephadex LH-20 with MeOH. The sugar fraction thus obtained was subjected to silica gel column chromatography (solv., $CHCl_3$–MeOH–H_2O, 8: 2: 0.2) to give a syrup with Rf 0.56 (solv. a), which was dried, methylated with DMF (0.5 ml), Ag_2O (0.5 g) and CH_3I (4 ml), and purified by silica gel column chromatography (solv. d) to yield a syrup of Rf 0.48 (solv. d), $[\alpha]_D$ −40.2° (c=5.09, $CHCl_3$). The PMR and EI-MS spectra were identical with those of per-O-methylapioside derived from the methanolysate of V.

Aglycone Tetramethylether (VI)——Amorphous (65 mg), $[\alpha]_D$ −201.2° (c=1.11, $CHCl_3$), Rf 0.19 (solv. d), EI-MS m/z: 532 (M^+).

2,3,5-Tri-O-Methyl-D-Apiofuranoside——Methyl 2,3,5-tri-O-methyl-β-D-apiofuranoside was hydrolyzed with 1 N HCl (11 ml), neutralized with 3% KOH–MeOH and passed through a Sephadex LH-20 column to give a methyl ether of Rf 0.49 (solv. b), $[\alpha]_D$ −14.5° (c=2.2, H_2O). EI-MS m/z: 175 ($C_8H_{15}O_4$, M–OH). The mixture of methylated sugars except for apioside was hydrolyzed as above and separated into the rhamnose, xylose and arabinose derivatives by silica gel column chromatography (45 g, solv. c).

2,4-Di-O-methyl-L-rhamnopyranose——A syrup (50 mg), Rf 0.35 (solv. b), $[\alpha]_D$ +7.9° (c=2.31, H_2O), EI-MS m/z: 192 ($C_8H_{16}O_5$, $M^{+\cdot}$).

2,3,4-Tri-O-methyl-D-xylopyranose——Colorless crystals (40 mg) from pet.ether–AcOEt, mp 89—91°, Rf 0.51 (solv. b); $[\alpha]_D$ +60.1°→+19.3° (13 hr later, c=1.34, H_2O). EI-MS m/z: 175 ($C_8H_{15}O_4$, M–OH).

4-O-Methyl-L-arabinopyranose——Colorless crystals (50 mg) from acetone, mp 103—104°, Rf 0.06 (solv. b); $[\alpha]_D$ +192.4°→+128.3° (13 hr later, c=2.23, H_2O). EI-MS m/z: 147 ($C_6H_{11}O_4$, M–OH).

Partial Hydrolysis of I giving VII——I (3.63 g) was refluxed with 0.2 N HCl–MeOH (20 ml) for 35 min on a bath, then neutralized with 3% KOH–MeOH. The salts were filtered off and the filtrate was evaporated to dryness *in vacuo* to give the residue, which was chromatographed on a silica gel column (120 g, sol., $CHCl_3$–MeOH–H_2O=7: 3: 0.2) to afford a white powder (2.80 g) from MeOH–acetone, mp 235—241° (dec.), Rf 0.20 (solv. a). $[\alpha]_D$ −112.4° (c=0.94, MeOH). *Anal.* Calcd for $C_{42}O_{62}O_{20}\cdot H_2O$: C, 55.74; H, 7.13. Found: C, 55.91; H, 7.12. IR ν_{max}^{KBr} cm^{-1}: 3650—3150 (OH), 1696, 1630 (enone), 976, 929, 875 (spiroketal). CD $[\theta]_{320}$ +3720 (c=0.032, EtOH, positive Cotton effect), UV λ_{max}^{EtOH} 247 nm (ε=6200), PMR ($CDCl_3$–CD_3OD) δ: 0.96 (3H, s, *tert.*CH_3), 1.08 (3H, d, *sec.*CH_3).

Methylation of VII giving VIII——A mixture of VII (1.0 g), DMF (10 ml), CH_3I (7 ml) and Ag_2O (2 g) was stirred overnight at room temperature. After usual work-up, this methylation was repeated twice. The syrup thus obtained was purified by silica gel column chromatography (50 g, solv., benzene–acetone=4: 1) to give amorphous VIII (620 mg) of Rf 0.39 (solv. c). $[\alpha]_D$ −100.2° (c=1.31, $CHCl_3$). *Anal.* Calcd for $C_{53}H_{84}O_{20}$: C, 61.13; H, 8.13. Found: C, 60.89; H, 8.06. IR ν_{max}^{KBr} cm^{-1}: 1705, 1630 (enone), 1200—1040 (ether). PMR ($CDCl_3$) δ: 0.93 (3H, d, J=6 Hz, 27-CH_3), 1.05 (3H, s, 19-CH_3), 1.29 (3H, d, J=7 Hz, rhamnosyl 6-CH_3), 3.37—3.61 (OMe), 4.22 (1H, d, J=6 Hz, arabinosyl 1-H), 4.28 (1H, d, J=6 Hz, 16-H), 4.38 (1H, d, J=6 Hz, xylosyl 1-H), 5.30 (1H, broad s, rhamnosyl 1-H), 5.60 (1H, broad d, 6-H). EI-MS m/z: 1040 ($M^{+\cdot}$), 531 ($C_{30}H_{43}O_8$), 384 ($C_{23}H_{28}O_5$), 353 ($C_{22}H_{25}O_4$), 317 ($C_{15}H_{25}O_7$), 264 ($C_{19}H_{20}O$), 189 ($C_9H_{17}O_4$), 175 ($C_8H_{15}O_4$).

Methanolysis of VIII——VIII (40 mg) was methanolyzed with 1 N HCl–MeOH (4 ml) for 1.5 hr on a hot bath. The methanolysate was treated in the usual manner, and subjected to TLC and GLC. TLC; solv. d. GLC; column temp. 155°, N_2 1.5 kg/cm². Methyl 2,3,4-tri-O-methyl-D-xylopyranoside, Rf 0.66 (β), 0.46 major (α), t_R 4′12″ (β), 5′36″ (α); methyl 2,3,4-tri-O-methyl-α-L-rhamnopyranoside, Rf 0.57 (α), t_R 4′18″ (α); methyl 4-O-methyl-L-arabinopyranoside Rf 0.10 (α and β).

Partial Hydrolysis of VIII giving IX——VIII (420 mg) was hydrolyzed with 0.2 N HCl–MeOH (8 ml) for 35 min on a hot bath, neutralized with 3% KOH–MeOH, and evaporated to dryness. Water was added to the residue to give a white precipitate. This was subjected to silica gel chromatography (40 g, benzene–acetone=2: 1) to collect the fraction of Rf 0.21 (solv. c), which was treated with dil.MeOH to give 190 mg of IX, amorph, $[\alpha]_D$ −98.3° (c=0.88, $CHCl_3$). *Anal.* Calcd for $C_{45}H_{70}O_{16}$: C, 62.33; H, 8.14. Found: C, 62.10; H, 8.21. EI-MS m/z: 866 ($M^{+\cdot}$), 335 ($C_{15}H_{27}O_8$), 189 ($C_9H_{17}O_4$).

Methylation of IX giving X——IX (150 mg) in $CHCl_3$ (5 ml) was stirred with CH_3I (6 ml) and Ag_2O (600

22) R.K. Hulyalker, J.K.N. Jones, and M.B. Perry, *Canad. J. Chem.*, **43**, 2085 (1965).

mg) overnight in the dark to give a syrup X (130 mg), with *Rf* 0.23 (solv. c). $[\alpha]_D$ −98.4° (*c*=1.21, $CHCl_3$). *Anal.* Calcd for $C_{46}H_{72}O_{16}$: C, 62.71; H, 8.24. Found: C, 62.98; H, 8.11. EI-MS *m/z*: 880 ($M^{+\cdot}$), 532 ($C_{30}H_{44}O_8$), 515 ($C_{30}H_{43}O_7$), 384 ($C_{23}H_{28}O_5$), 353 ($C_{22}H_{25}O_4$), 349 (penta-O-methyl terminal rhamnosyl-arabinosyl cation), 264 ($C_{19}H_{20}O$), 189 (tri-O-methyl terminal rhamnosyl cation), 157.

Methanolysis of X——X (110 mg) was methanolyzed with 1 N HCl–MeOH (6 ml) for 1.5 hr on a hot bath, neutralized with 3% KOH–MeOH and passed through a Sephadex LH-20 column (MeOH) to give the methanolysate, which was subjected to TLC and GLC. TLC: solv., benzene-acetone 2: 1. GLC: column temp., 185°, N_2 1.5 kg/cm². Methyl 2,3,4-tri-O-methyl-α-L-rhamnopyranoside, *Rf* 0.66, t_R 1′8″; methyl 3,4-di-O-methyl-L-arabinopyranoside, *Rf* 0.24 (β), 0.20 (α), t_R 4′42″ (β).

Partial Hydrolysis of VII giving XI, XII and XIV——VII (1.5 g) in 0.5 N HCl–MeOH (15 ml) was refluxed for 15 min on a hot bath. The resulting hydrolysate was separated by silica gel chromatography (150 g, solv., $CHCl_3$–MeOH–H_2O=8: 2: 0.3→7: 3: 0.2) to give XI (*Rf* 0.29, solv. a, 110 mg), XII (*Rf* 0.38, 180 mg) and XIV (*Rf* 0.31, 90 mg).

XI: amorphous, $[\alpha]_D$ −117.9° (*c*=0.84, MeOH). *Anal.* Calcd for $C_{37}H_{54}O_{16}\cdot 2H_2O$: C, 56.19; H, 7.39. Found: C, 56.31; H, 7.44. PMR ($CDCl_3$–CD_3OD–D_2O+CF_3COOH) δ: 4.26 (1H, m, arabinosyl 1-H), 4.50 (1H, d, *J*=7 Hz, 16-H) 5.32 (1H, s, rhamnosyl 1-H). Hydrolysis of XI gave II, arabinose and rhamnose (TLC and PPC).

XII: mp 223—226° (colorless needles from dil.MeOH), $[\alpha]_D$ −142.4° (*c*=0.78, MeOH). *Anal.* Calcd for $C_{31}H_{44}O_{12}\cdot H_2O$: C, 59.41; H, 7.40. Found: C, 59.20; H, 7.48. PMR ($CDCl_3$–CD_3OD–D_2O+CF_3COOH): 4.22 (1H, m, arabinosyl 1-H), 4.44 (1H, d, *J*=6 Hz, 16-H). Hydrolysis of XII gave II and arabinose (TLC and PPC).

XIV: Amorphous $[\alpha]_D$ −109.8° (*c*=0.74, MeOH), $[M]_D$ −812°. *Anal.* Calcd for $C_{36}H_{52}O_{16}\cdot H_2O$: C, 56.98; H, 7.17. Found: C, 57.20; H, 7.16. PMR ($CDCl_3$–CD_3OD–D_2O) δ: 4.30 (1H, m, arabinosyl 1-H), 4.47, 4.54 (1H each, both d with *J*=7 Hz, 16-H and xylosyl 1-H). Hydrolysis of XIV gave II, xylose and arabinose.

3,21,23,24-Tetra-O-methyltrillenogenin Monoacetate (XIII)——VI (50 mg) was acetylated with Ac_2O-pyridine (1: 1, 10 ml) in the usual manner to give XIII (53 mg), mp 171—174° (colorless plates from MeOH), $[\alpha]_D$ −210° (*c*=1.12, $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (OAC), 1705, 1630 (enone), 1140, 1080 (ether). PMR ($CDCl_3$) δ: 0.93 (3H, d, *J*=6.0 Hz, 27-CH_3), 1.12 (3H, s, 19-CH_3), 2.12 (3H, s, OAc), 3.35, 3.37, 3.52, 3.56 ($OCH_3\times 4$), 4.30 (1H, d, *J*=6.0 Hz, 16-H), 4.65 (1H, q, *J*=4.5, 11.5 Hz, 1-H), 5.65 (1H, broad d, *J*=6.0 Hz, 5-H). EI–MS *m/z* 574 ($C_{32}H_{46}O_9$, $M^{+\cdot}$).

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