The melting point of **2a** was not depressed by admixture with authentic specimen of 12-epirubijervine which was synthesized according to the method of Pelletier,[5] and **2a** was identified as 12-epirubijervine [(22*R*,25*S*)-solanid-5-ene-3β,12β-diol].

No pertinent biogenetic researches for jervanine and veratranine alkaloids on plants have been reported. **2a** corresponds to the starting material of Narayanan's hypothesis of C-nor-D-homo rearrangement[6] and **1a** coincides with the compound cleaved at C-16-N bond, after C-nor-D-homo rearrangement from **2a**, except the orientation at C-21 methyl group. However, the reversion of C-21 methyl group from **2a** to **1a** still remains uncertain.

The authors are indebted to Dr. N. Kamijyo, Government Industrial Research Institute, Osaka, for the use of the diffractometer.

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Received July 27, 1979

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[Chem. Pharm. Bull. 27(10)2536—2538(1979)]

UDC 547.914.02.04 : 546.819.04

The Constituents of *Schizandra chinensis* Baill.[1] The Cleavage of the Methylenedioxy Moiety with Lead Tetraacetate in Benzene, and the Structure of Angeloylgomisin Q

Cleavage of the methylenedioxy moiety with lead tetraacetate in benzene to diphenol was described. Piperonylic acid methyl ester (**5**), 3,4-methylenedioxytoluene (**6**), 2,3-methylenedioxyanisole (**7**) and gomisin A (**8**) afforded protocatechuic acid (**10**), 3,4-dihydroxytoluene (**11**), 2,3-dihydroxyanisole (**12**) and compound **13**, respectively, by the reaction. The structure of angeloylgomisin Q, isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae), was elucidated as **4** with the aid of the above reaction.

Keywords——cleavage of methylenedioxy moiety; lead tetraacetate; *Schizandra chinensis* Baill.; Schizandraceae; dibenzocyclooctadiene lignan; angeloylgomisin Q

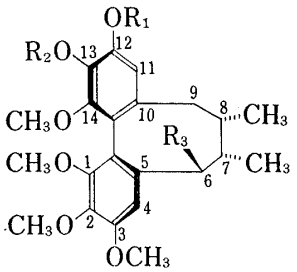
In the course of the studies on the constituents of *Schizandra chinensis* Baill. (Schizandraceae), we have found that treatment of gomisin N(**1**) with lead tetraacetate [$Pb(OAc)_4$] in AcOH gave 6β-acetoxygomisin N(acetylgomisin O, **2**), but treatment of **1** with the reagent in dry benzene gave an unexpected diphenol (**3**).[1] This communication deals with the further cleavage reactions of the methylenedioxy moiety with $Pb(OAc)_4$ in dry benzene, and also describes the structure elucidation of a new lignan, angeloylgomisin Q, isolated from the fruits of the same plant.

1) Y. Ikeya, H. Taguchi, I. Yosioka, and H. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), in press.

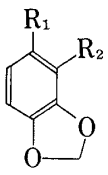
Table I. Cleavage of the Methylenedioxy Moiety with $Pb(OAc)_4$

Starting material (mg)	Reaction conditions: $Pb(OAc)_4$ mg	Benzene ml	Temperature °C	Time hr	Product mg (%)	Recovery of starting material mg (%)
5(180)	531	8	60	20	**9**(44 mg)→**10**, 32(19)	114(63)
6(105)	410	6	70	7	**11**, 35(40)	14(13)
7(152)	531	8	60	7	**12**, 35(25)	91(59)
8(150)	300	5	50	7	**13**, 28(19)	49(32)

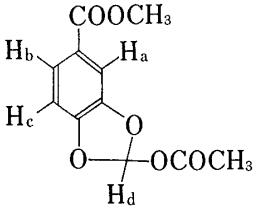
All the products (**10**—**13**) gave corresponding dimethyl ethers on treatment with $(CH_3)_2SO_4$ and K_2CO_3 in acetone, therefore gomisin A (**8**) was correlated with schizandrin (**14**).[2]



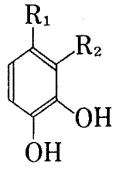
1: $R_1+R_2=CH_2$, $R_3=H$
2: $R_1+R_2=CH_2$, $R_3=CH_3COO-$
3: $R_1=R_2=R_3=H$



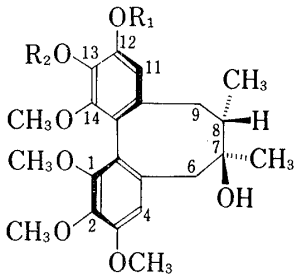
5: $R_1=COOCH_3$, $R_2=H$
6: $R_1=CH_3$, $R_2=H$
7: $R_1=H$, $R_2=OCH_3$



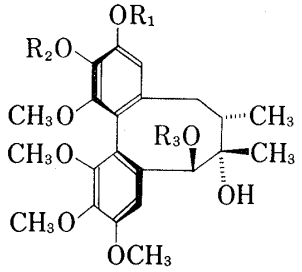
9



10: $R_1=COOCH_3$, $R_2=H$
11: $R_1=CH_3$, $R_2=H$
12: $R_1=H$, $R_2=OCH_3$



8: $R_1+R_2=CH_2$
13: $R_1=R_2=H$
14: $R_1=R_2=CH_3$



4: $R_1=R_2=CH_3$, $R_3=\begin{matrix}CH_3\\H\end{matrix}\!\!>C=C<\!\!\begin{matrix}CO-\\CH_3\end{matrix}$
15: $R_1=R_2=CH_3$, $R_3=H$
16: $R_1+R_2=CH_2$, $R_3=H$
17: $R_1=R_2=H$, $R_3=CH_3CO-$
18: $R_1=R_2=CH_3$, $R_3=CH_3CO-$

Chart 1

Piperonylic acid methyl ester (**5**), 3,4-methylenedioxytoluene (**6**), 2,3-methylenedioxyanisole (**7**) and gomisin A (**8**) were submitted to the reaction. The reaction conditions and yields of the corresponding diphenols are shown in Table I. In the above compounds, **5** gave compound **9** as an amorphous powder [proton nuclear magnetic resonance (^1H NMR) spectrum (δ in $CDCl_3$): 2.13 (3H, s, $COCH_3$), 3.90 (3H, s, $COOCH_3$), 7.00 (1H, d, J=8.5 Hz, $H_{(c)}$), 7.62 (1H, d, J=2 Hz, $H_{(a)}$), 7.77 (1H, d,d, J=8.5/2 Hz, $H_{(b)}$), 7.75 (1H, s, $H_{(d)}$), hydrolysis of which with 80% AcOH at room temperature for 1 hr gave protocatechuic acid (**10**). The above observation suggests that the reaction might proceed *via* a displacement of proton of methylenedioxy moiety by an acetoxy group, followed by hydrolysis during separation of the product. So far as we know, this is the first cleavage reaction of the methylenedioxy moiety with $Pb(OAc)_4$.

Angeloylgomisin Q (**4**) was isolated as colorless prisms, $C_{29}H_{34}O_{10}$, mp 82.5—83.5°, $[\alpha]_D^{24}$ −26.4° (c=1.10, $CHCl_3$) (yield 0.0047%). Infrared (IR) spectrum ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1700 (C=O), 1642 (C=C), 1596, 1581 (aromatic). Ultraviolet (UV) spectrum λ_{max}^{EtOH} nm (log ε):

220 (4.74), 250—251 (sh 4.17), 285—286 (sh 3.45). MS *m/e* (%): 530 (M^+, 17), 430 ($M^+ - CH_3CH{=}C(CH_3)COOH$, 14), 387 (16), 359 (45), 83 ($CH_3CH{=}C(CH_3)CO^+$, 100), 55($CH_3CH{=}C^+ - CH_3$, 69). ^{1}H NMR (δ in $CDCl_3$): 1.17 (3H, d, J=7 Hz, C<u>H</u>$_3$–ĊH), 1.30 (3H, s, C<u>H</u>$_3$–Ċ–OH), 1.57 (1H, s, OH), 1.87 (1H, m, –ĊH), 2.25 (center) (2H, m, Ar–C<u>H</u>$_2$–), 3.52 (3H, s), 3.55 (3H, s), 3.82 (3H, s), 3.87 (3H, s), 3.88 (6H, s) (6×OCH_3), 5.77 (1H, s, $C_{(6)}$–H), 6.53 (1H, s, $C_{(11)}$–H), 6.80 (1H, s, $C_{(4)}$–H), 1.30 (3H, m), 1.80 (3H, d, q, J=7/1 Hz), 5.95 (1H, q, q, J=7/1 Hz) (angeloyl group).

The above spectral data suggested that **4** is a dibenzocyclooctadiene lignan having six methoxyls on the aromatic rings, an angeloyl group, a secondary methyl and a tetriary methyl attached to carbon carrying a hydroxy group. On hydrolysis with 3% KOH–EtOH, **4** afforded a diol (**15**), named gomisin Q, and an acid. The former was obtained as colorless needles (from ether–*n*-hexane), $C_{24}H_{32}O_8$, mp 191—193°, $[\alpha]_D^{22}$ −106° (c=1.24, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3410, 3370 (OH), 1595, 1575 (aromatic). ^{1}H NMR (δ in $CDCl_3$): 1.15 (3H, d, J=7 Hz, C<u>H</u>$_3$–ĊH), 1.40 (3H, s, C<u>H</u>$_3$–Ċ–OH), 1.65 (1H, d, J=11 Hz, OH, D_2O exchangeable), 1.82 (1H, m, –ĊH), 2.12 (1H, d, d, J=13.5/2 Hz, $C_{(9\beta)}$–H), 2.38 (1H, d, d, J=13.5/8.5 Hz, $C_{(9\alpha)}$–H), 3.63 (3H, s), 3.72 (3H, s), 3.88 (3H, s), 3.92 (9H, s) (6×OCH_3), 4.57 (1H, d, J=11 Hz, $C_{(6)}$–H, singlet on addition of D_2O), 6.58 (1H, s, $C_{(11)}$–H), 6.62 (1H, s, $C_{(4)}$–H). The latter was identified as a mixture of angelic acid and tiglic acid by gas chromatography (during hydrolysis, a portion of angelic acid was isomerized to tiglic acid). The upfield shift of $C_{(6)}$-proton in ^{1}H NMR spectrum of **15**, compared with that of **4**, showed that the angeloyl group in **4** links to the $C_{(6)}$-hydroxy group of **15**. The structure of **4** was confirmed by correlation with deangeloylgomisin B (**16**)[2] as described below.

Treatment of acetyldeangeloylgomisin B (**16**, R_3=$COCH_3$) (84 mg) with $Pb(OAc)_4$ (126 mg) in dry benzene (4 ml) afforded a compound **17** (11.5 mg) [^{1}H NMR (δ in $CDCl_3$): 5.53 (2H, s, 2×phenolic OH), 3.31 (3H, s), 3.53 (3H, s), 3.93 (6H, s) (4×OCH_3), no methylenedioxy signal], which was methylated with $(CH_3)_2SO_4$ and K_2CO_3 in dry acetone to give compound **18** as an amorphous powder [^{1}H NMR (δ in $CDCl_3$): 3.57 (3H, s), 3.70 (3H, s), 3.87 (3H, s), 3.93 (9H, s) (6×OCH_3)]. Hydrolysis of **18** afforded **15**, colorless needles, $C_{24}H_{32}O_8$, mp 190—192.5°, $[\alpha]_D^{23}$ −96.5° (c=0.508, $CHCl_3$), which was identified as gomisin Q (**15**) by direct comparison (IR, mixed mp, ^{1}H NMR and $[\alpha]_D$). The structure of angeloylgomisin Q was thus elucidated as **4**.

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Received August 9, 1979

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