Communications to the Editor

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Isolation of $\Delta^{3,5}$-Desoxytigogenin (25D-Spirosta-3,5-diene) from some Dioscoreaceae Plants

Crude sapogenins obtained from four kinds of Dioscoreaceae plant were shown[1] by paper chromatography to contain a minor amount of unknown substance (I) (Rf 0.96∼0.98, reddish pink coloration by $SbCl_3$), besides diosgenin (Rf 0.68, pink). Rf value and coloration of (I), in comparison with those of diosgenin and β-sitosterol (Rf 0.80∼0.81, pink), suggested that it would be a new unsaturated steroid, possibly without a hydroxyl group.

In the course of our study on the saponins from *Dioscorea septemloba* THUNB., *D. Tokoro* MAKINO, and *D. nipponica* MAKINO, (I) has also been detected and now isolated with the aid of chromatography from each sapogenin mixture obtained from the defatted methanol extracts or crude saponins upon hydrolysis with 2*N* or 4*N* hydrochloric acid in 50% ethanol for 3∼5 hours.

Physical constants and some properties of (I) are as follows : m.p. 164∼165°, $[\alpha]_D^{17}$ −178°($CHCl_3$); U.V. λ_{max}^{EtOH} mμ (log ε) : 228(4.43), 235(4.46), 243(4.27); I.R. λ_{max}^{Nujol} 10.18, 10.89, 11.12, 11.57 μ. *Anal.* Calcd. for $C_{27}H_{40}O_2$: C, 81.76; H, 10.17; mol. wt., 396. Found : C, 81.39; H, 10.15; mol. wt., 397. Rf : 0.98 (solvent system : petr. ether • toluene • EtOH • water = 40:5:1:9), 0.02 (developed with ethylcellosolve • *n*-PrOH • MeOH • water = 35:10:30:10 on paraffine-impregnated paper); Liebermann-Burchard reaction, wine-red turning to brown; Kariyone-Hashimoto reaction, reddish purple (at 50°); digitonin reaction, no precipitation; acetylation with Ac_2O and pyridine, material recovered unchanged.

From these data it seemed most probable that (I) is 25D-spirostane with 3,5-conjugated double bonds and no hydroxyl group. Subsequently (I) has been identified as $\Delta^{3,5}$-desoxytigogenin (25D-spirosta-3,5-diene) (II) by comparisons of its optical rotation, Rf value, and absorption spectra as well as by mixed fusion with the specimen synthesized from diosgenin by the method of Wall and Serota,[2] m.p. 164°, $[\alpha]_D^{11}$ −177° ($CHCl_3$); U.V. λ_{max}^{EtOH} mμ (log ε) : 228(4.28), 235(4.31), 243(4.09); I.R. λ_{max}^{Nujol} μ : 10.17, 10.88, 11.10, 11.56. *Anal.* Calcd. for $C_{27}H_{40}O_2$: C, 81.76; H, 10.17. Found : C, 81.50; H, 10.25. Rf 0.96. Dioscin[3] and diosgenin have also been proved by paper chromatography to afford (II) under similar conditions and unexpectedly the hydroxyl group at C-3 of diosgenin seemed to have been eliminated to form a dienic system even in this rather mild condition. Wall, Serota, and Witnauer[4] reported that (II) was formed from yamogenin (25L-analog of diosgnein) by treatment with 2*N* hydrochloric acid. The procedure, however, included a prolonged heating (96 hours).

Therefore, taking account of the condition of hydrolysis, (II) obtained from the Dioscoreaceae plants in this study may be an artifact formed during the hydrolytic cleavage of diosgenin glycosides.

According to the latest report,[5] the saponin from *Dioscorea barbasco* AMARILLO, containing only diosgenin as a sapogenin constituent, was hydrolyzed with 4*N* hydrochloric acid for 4 hours to give a sapogenin (III), m.p. 165∼175°. It is possible that (III)

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1) T. Tsukamoto, T. Kawasaki : J. Pharm. Soc. Japan, **74**, 72(1954).
2) M. E. Wall, S. Serota : J. Am. Chem. Soc., **78**, 1747(1956).
3) M. E. Wall, S. Serota, L. P. Witnauer : *Ibid.*, **77**, 3086(1955).
4) T. Tsukamoto, T. Kawasaki, T. Yamauchi : This Bulletin, **4**, 35(1956).
5) J. W. Rothrock, P. A. Hammes, W. J. McAleer : Ind. Eng. Chem., **49**, 176(1957).

might be a mixture consisting of diosgenin along with a considerable amount of (II).

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Studies on Digitalis Glycosides. Acetylgitoxin-α from Gitoxin

Acetylgitoxin-α had been obtained from lanatoside-B by means of enzymatic decomposition by Stoll *et al.*[1] We prepared the same compound from gitoxin by means of partial acetylation.

Gitoxin was acetylated for 16 hours with equimolar amount of acetic anhydride in pyridine solution at room temperature, the crude acetate was submitted to silica-gel chromatography, and the main fraction eluted with $CHCl_3 \cdot MeOH$ (25:1) was recrystallized from $EtOH \cdot Et_2O$ to colorless plates, m.p. 190~202°/246~249°.[2] Analytical values corresponded to those of monoacetylgitoxin (*Anal.* Calcd. for $C_{43}H_{66}O_{15} \cdot H_2O$: C, 61.40; H, 8.15; $COCH_3$, 5.11. Found : C, 60.99; H, 8.25; $COCH_3$, 5.52). The results of comparison of this product with authentic sample of acetylgitoxin-α, kindly furnished by Prof. A. Stoll, indicated the identity of the two glycosides as follows:

	Acetylgitoxin-α	Monoacetylgitoxin obtained here	Mixture
m.p.	190~203°/245~248° [2]	190~202°/246~249°	190~202°/245~249°
Rf ($HCONH_2$, $MeCOEt \cdot Xylene = 1:1$)	0.51	0.51	0.51
($HCONH_2$, $BuOH \cdot Toluene = 1:6$)	0.53	0.53	0.53
$[\alpha]_D^{30}$	+16° [1] (pyridine)	+17.5° (pyridine)	

The infrared spectrum of both also agreed well. It is presumable that acetyldigitoxin-α and acetyldigoxin-α could be prepared by a similiar procedure from digitoxin and digoxin, respectively, and the studies about it are in progress.

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[1] A. Stoll, W. Kreis : Helv. Chim. Acta, **17**, 592(1934); A. Stoll, A. von Wartburg, W. Kreis: *Ibid.*, **35**, 1324(1952).

[2] Though m.p. of acetylgitoxin-α had been reported as 203~204° [1], we found it showed the above-mentioned double melting point.