생 약 학 회 지
Kor. J. Pharmacog.
3(1) : 21~22(1972)

A New Diterpenic Glucoside of *Siegesbeckia pubescens*

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희첨의 새로운 Diterpene 배당체에 관하여

金 濟 勳
서울대학교 생약연구소

우리 나라 漢方療法에서 高血壓治療에 널리 쓰이고 있는 豨薟은 털진득찰 *Siegesbeckia pubescens*의 全草로서 그 有效成分으로서는 이미 物質 A[1] $C_{20}H_{34}O_4$ mp 192~193° $[\alpha]_D^{20}$ -22 (in dioxane), B[2] $C_{20}H_{32}O_4$ 260.2° $[\alpha]_D^{20}$ -88 (in pyridine)의 化學構造 및 生理作用을 밝힌 바 있다.

본 연구에서는 또하나의 새로운 配糖體 compound(I) $C_{26}H_{44}O_8$ mp 225~6° $[\alpha]_D^{20}$ -40을 얻어 그의 理化學的 性狀 및 誘導體의 合成으로서 化學構造를 究明하였다.

A New diterpene glucoside(I) {$C_{26}H_{44}O_8$ mp. 225~6° (EtOH), $[\alpha]_D^{20}$-40(c.1% EtOH). IR: ν_{max}^{KBr} cm^{-1} 3330, 1060, 1020, 1075 (OH), 1670 (>C=C—H), 1650 (C=C) 850, 840 one pair of bonds (RR'C=CR''H) 1380, 1365 doublet (>C—CH_3CH_3), 1195 (>C<). NMR(τ): 5.2*bs*. (>C=—H—C—) 0.83, 1.05 (CH_3)} was isolated from methanol extract of *Siegesbeckia pubescens*.

Acetylation of (I) with acetic anhydride and pyridine at room temperature afforded a hexaacetate(II) {$C_{38}H_{56}O_{14}$ mp, 128°(EtOH), $[\alpha]_D^{20}$ -43.2(C. 1% MeOH). IR; ν_{max}^{KBr} cm^{-1} 1735 (O=—C—O—), 1240. NMR (τ): 5.3*bs* (>C=C—H) 0.85, 1.03(CH_3)}.

Hydrolysis of (I) with β-glucosidase at 36° for 60 hours gave 1 mole of glucose(glucoosazone mp 208°) and an aglycone(III) {$C_{20}H_{34}O_3$ mp 163°(EtOH), $[\alpha]_D^{20}$-10(c. 1% EtOH) IR: ν_{max}^{KBr} cm 3280, 1085, 1060, 1030, 1015 (OH), 1455, 1380, 1365 doublet (>CCH_3 CH_3), 1195 (=C=1675 (RR'C=C——R''H), 1640 (C=C), 855, 838 one pair of bonds (RR'C=CR''H). NMR(τ): 5.2*bs* (>C=C—H), 0.83, 1.0(CH_3)}.

Oxidation of (III) with sodium metaperiodate gave formaldehyde together with nor-aldehyde(IV) {$C_{19}H_{30}O_2$ mp. 114.5(EtOH). $[\alpha]_D^{20}$-77(c. 1% EtOH). IR: ν_{max}^{KBr} cm^{-1} 3280, 1085, 1035 (OH), 1720 (O=C—H), 2,720 (—CHO:δCH)}. The IR spectra show that a hydroxyl group of nor-aldehyde is secondary.

Huang-Minlon reduction of the nor-aldehyde(IV) gave a mono-nor-alcohol(V) {$C_{19}H_{32}O$ mp 137 5 $[\alpha]_D^{20}$ -40(EtOH), ν_{max}^{KBr} cm^{-1} 3200, 1085, 1025 (OH), 1670 (RR'C=CR''H), 1640 (C=C) 1455 1380, 1355 doublet (>C——CH_3CH_3), 1195 (>C<), 862, 858 one pair of bonds RR''>C=CR''H. NMR (τ): 5.2*bs* (>C=C—H), 0.8, 0.81, 0.92, 1.0(CH_3)}.

Oxidation of mono-nor-alcohol(V) with Sarett reagent gave a ketone(VI) {$C_{19}H_{30}O$ mp. 97~8°, $[\alpha]_D^{20}$ -43.5 (EtOH), ν_{max}^{KBr} cm^{-1} 3320 (overtone), 1695 (>C=O), 1100 (ali. ketone) 1425cm^{-1} (anactive methylene group is also present). NMR (τ): 0.95, 0.97, 1.0, 1.08 (CH_3), 5.27*bs*(>C=C—H), 2.87*d*. 2.66*d*. (J=12.75 c/s, 1 H part A of an AB system)}.

A reduction product of the ketone(VI) by Huang-Minlon method was identified with $C_{19}H_{32}$(VII) mp 42°, $[\alpha]_D^{20}$ -28.72, which was derived from compound A.

This evidence, together with the spectral and chemical data of (I) and (III), suggests that the partial structure of the aglycone is as shown in CHART I.

NMR spectra of the ketone (VI) show two lines at 2.89 and 2.66(J=12.75c/s, IH part A of an AB

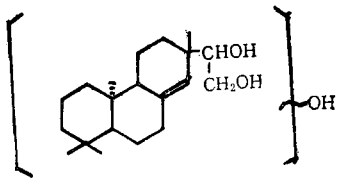

Chart I

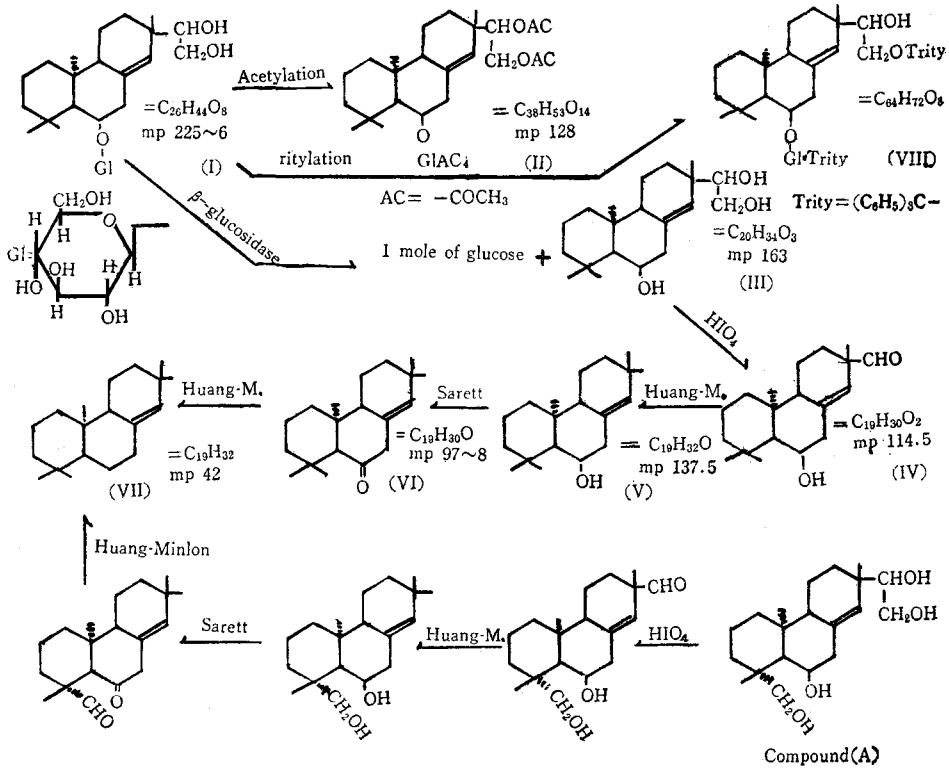

Chart (II) Derivatives of glycoside and aglycones

system). These can be attributed to one proton of a methylenic group both allylic and adjacent to a carbonyl function. This fact indicates that the secondary hydroxyl function is located at C_6.

The facts that oxidation of (I) with sodium metaperiodate in ethylalcohol solution gives formaldehyde, and tritylation of (I) affords ditritylether (VIII) $C_{64}H_{72}O_8$, mp 115~116, indicated that the glucose moiety is combined at the C_6 hydroyl group of the aglycone.

Acknowledgments

The author wishes to thank Professors K. D. Han and L. K. Woo for their encouragement and advice and Miss S. J. Oh for technical assistance.

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