A NOVEL DITERPENE GLUCOSIDE FROM PHASEOLUS COCCINEUS[1)]

Masami YAMASHITA,[a] Junei KINJO,[a] Yumiko ITO,[a] Tetsuya KAJIMOTO,[a] Nobuhiro MARUBAYASHI,[b] Ikuhiko UEDA,[b] and Toshihiro NOHARA*,[a]

Faculty of Pharmaceutical Sciences, Kumamoto University,[a] Oe-honmachi 5-1, Kumamoto 862, Japan and Yoshitomi Pharmaceutical Co., Ltd.,[b] 955 Koiwai, Yoshitomi-cho, Chikujo-gun, Fukuoka 871, Japan

The structure of a new seco-ent-kaurane diterpene glucoside, named coccinin, isolated from the beans of Phaseolus coccineus, has been established.

KEYWORDS Phaseolus coccineus; Leguminosae; seco-ent-kaurane; diterpene; coccinin; X-ray analysis

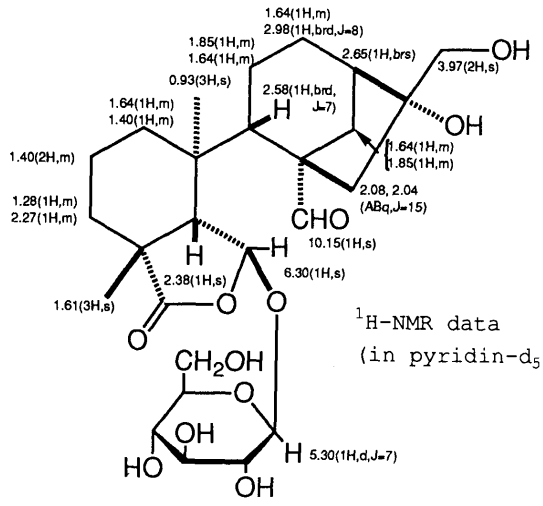
Gibberellin A_1 has been known as one of the ingredients of Phaseolus coccineus L,.[2)] During our studies on the constituents of leguminous plants, we have found a novel seco-ent-kaurane diterpene glucoside along with an oleanene tetraglycoside. This paper is concerned with the structure of diterpene glucoside.

A diterpene, $C_{26}H_{40}O_{11}$, named coccinin was obtained as colorless plates from water sat. 1-butanol, mp 190-193°C, $[\alpha]_D$ +19.9°(MeOH), in a 0.025% yield from the methanolic extract (110 g) of the dried commercial beans (1.98 kg). The IR spectrum of coccinin showed absorptions due to strong hydroxyl (3448 cm^{-1}), γ-lactone ring (1780 cm^{-1}) and carbonyl groups (1706 cm^{-1}). A negative FAB-MS indicated a molecular ion peak at m/z 527 and a peak due to $[M\text{-hexose}]^-$ at m/z 365. The ^{1}H-NMR spectrum (pyridine-d_5) showed signals due to two methyl groups (δ 0.93, s and 1.61, s), one hydroxymethyl group (δ 3.97, 2H, s), a hemiacetal proton (δ 6.30, s), a hexosyl anomeric proton (δ 5.30, d, J=7.4 Hz) and an aldehyde proton (δ 10.15, s). The ^{13}C-NMR spectrum disclosed twenty six carbon signals consisting of two methyl groups (δ 21.9, 30.1), eight methylene groups (δ 18.2, 20.1, 26.0, 31.0, 31.1, 33.6, 47.8 and 65.7), three methine carbons (δ 45.8, 47.7 and 54.2), one hemiacetal carbon (δ 104.7), four quaternary carbons (δ 39.9, 40.8, 59.2 and 81.1), two carbonyl carbons [δ 181.5 (s) and 205.8 (d)] together with a β-D-glucopyranosyl moiety (δ 104.9, 75.2, 79.2, 71.0, 78.4, 62.1: C-1-C-6).

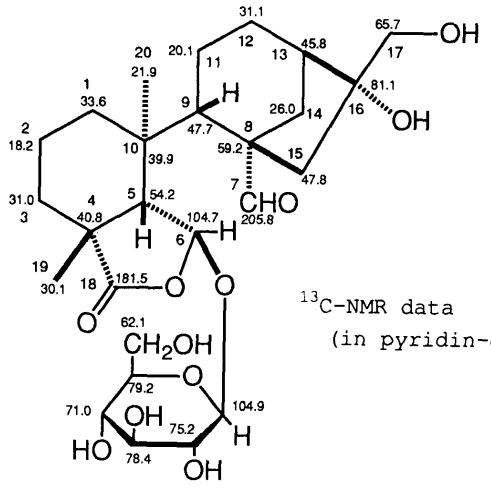
To determine the structure, the single crystal of coccinin was subjected to X-ray diffraction analysis. The crystal data were orthorhombic, space group $P2_12_12_1$, Z=4, a=12.027(1), b=31.315(3), c=7.227(1) Å, V=2721.6(4) Å^3, Dx=1.377 Mgm^{-3}, μ(CuKα)=0.885 mm^{-1}. All data were collected on an Enraf-Nonius CAD 4F-11 diffractometer using Cu-Kα radiation and a graphite monochrometer. The structure was solved by direct methods and refined by least-squares to an R factor of 0.039 for 2264 reflections. The crystallographically derived structure of coccinin was represented as ent-6β,16α,17-trihydroxy-7,18-dioxo-6,18-epoxy-6,7-seco-kaurane 6-O-β-D-glucopyranoside as shown in Fig. 1.

The structure is of interest in that the C-6 carbon is a hemiacetal center with a glucosidic linkage and the double bond between C-16 and C-17 was hydroxylated.

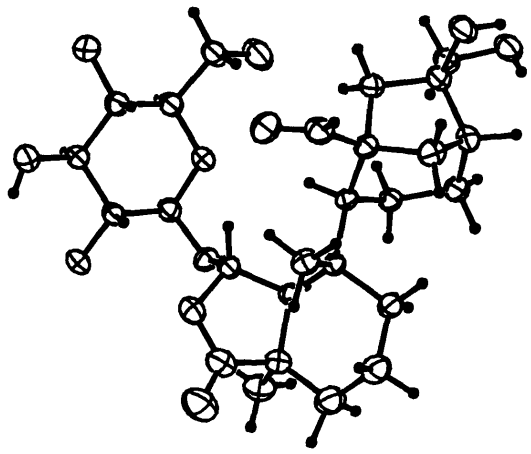
Coccinin showed no growth effect on the rice seeds, Oryza sativa.



^{1}H-NMR data
(in pyridin-d_5)



^{13}C-NMR data
(in pyridin-d_5)



ORTEP drawing of coccinin

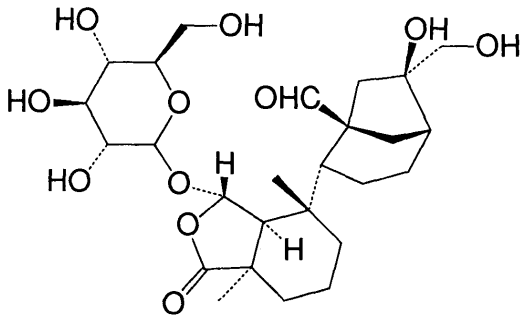


Fig. 1. Structure of Coccinin

REFERENCES AND NOTES

1) Part XVIII in the series of the studies on the constituents of the leguminous plants.

2) J.MacMillan and P.J.Suter, Naturwissenschaften, **45**, 46 (1958).

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