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ISOLATION OF A NEW MONOTERPENE CONJUGATED TRITERPENOID FROM THE STEM BARK OF *ALBIZZIA JULIBRISSIN*

WON SICK WOO and SAM SIK KANG

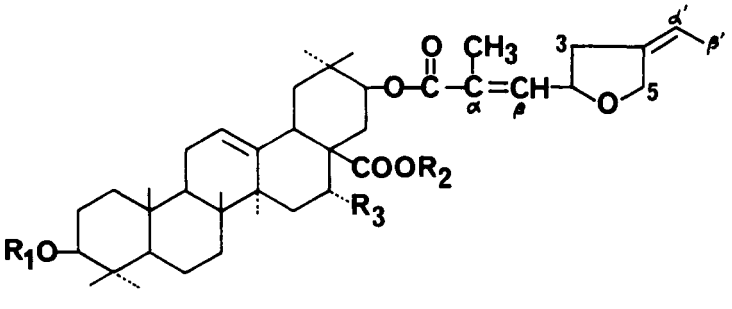
Natural Products Research Institute, Seoul National University, 28 Yun-keun Dong, Chong-no Ku, Seoul 110, Korea

It was previously demonstrated that the saponin fraction from the stem bark of *Albizzia julibrissin* Durazz. (Leguminosae) stimulated uterine muscle contractions (1). Four pentacyclic triterpenoids, acacic acid lactone, machaerinic acid lactone, machaerinic acid methylester, and acacigenin B were isolated from the acid hydrolyzate of the fraction (2,3). This paper deals with the isolation and structure elucidation of a new sapogenin (**1**) from the same source.

The sapogenin mixture, on chromatographic separation, afforded **1**, mp 258-262°, as a minor component. Compound **1** showed positive Liebermann-Burchard and tetranitromethane tests and uv absorption maximum at 215 nm (log ε 4.02), indicating the presence of an α,β-unsaturated ester function (3,4). This was further corroborated by its ir spectrum, which showed peaks at 1703 and 1650 cm^{-1} (α,β-unsaturated ester). The compound **1** on treatment of CH_2N_2 yielded a monomethylester **2**, mp 139-141°, which on acetylation with Ac_2O-pyridine at room temperature gave a monomethyl monoacetate **3**, mp 219-222°. On saponification under reflux with alcoholic KOH, **1** furnished machaerinic acid mp 306°, and 4-(ethylidene)-2-tetrahydrofuranmethacrylic acid (TFA), mp 118-120°, which were identified by direct comparisons with authentic samples (3). The nmr spectrum of **3** showed seven angular methyl groups at δ 0.71-1.27, one acetoxyl signal at 2.03, a methylester signal at 3.59, and other signals (see Experimental) reminiscent of those (3) of acacigenin B methyl acetate (**4**).

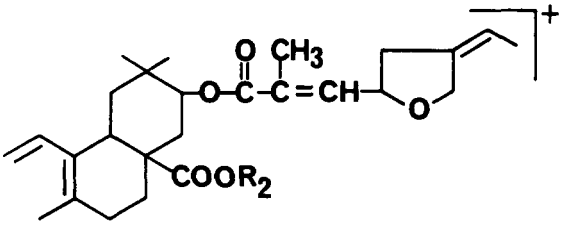
The above data together with the failure of lactonization of **1** during the acid treatment of the saponin suggested that TFA was linked to the hydroxyl group at C-21 in machaerinic acid.

This suggestion was confirmed from the mass spectral fragmentation patterns of the compounds, **1, 2,** and **3**. All the compounds exhibited molecular ion peaks at *m/z* 636, 650, and 692, respectively. These ion peaks are accompanied by fragments (i.e., *m/z* 454, 468, and 510, respectively) 182 mass units ($C_{10}H_{14}O_3$) lower. Retro-Diels-Alder fragmentation of the molecules produced small but prominent peaks (species **a**) at *m/z* 428 for **1** and 442 for **2** and **3**, re-

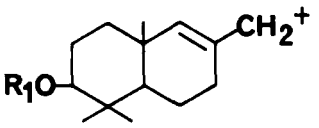


1 $R_1=R_2=R_3=H$
2 $R_1=H$ $R_2=Me$ $R_3=H$
3 $R_1=Ac$ $R_2=Me$ $R_3=H$
4 $R_1=Ac$ $R_2=Me$ $R_3=OH$

spectively, from which TFA was lost to give intense peaks at *m/z* 246 for **1** and 260 for **2** and **3**, respectively, and subsequent loss of the substituents at C-17 yielded fragments with the same mass (*m/z* 201). As expected, fragments (species **b**) composed of rings A and B were found at *m/z* 207 for **1** and **2** and 249 for **3**, respectively; in all cases, an *m/z* 189 fragment due to further loss of H_2O or HOAc from species **b** could be observed.



a



b

From the above data, **1** was established as 21-[4-(ethylidene)-2-tetrahydrofuranmethacryloyl] machaerinic acid. To our best knowledge, this compound has not been previously reported in the literature.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Mitamura-Riken apparatus and are uncorrected. The uv spectra were measured with Gilford System 2600 spectrophotometer, and the ir spectra were recorded with Perkin-Elmer 283B spectrophotometer. Optical rotations were obtained on a Rudolph Autopol III automatic polarimeter and pmr spectra were recorded at 80 MHz on a Varian FT-80A with TMS as internal standard. Mass spectra were taken on a Hewlett-Packard 5985B gc/ms spectrometer operating at 70 eV. Tlc was run on silica gel F_{254} plates, and the following solvents were employed; (a) C_6H_6-Et_2O-MeOH (16:4:1), (b) C_6H_6-Et_2O (9:1).

PLANT MATERIAL.—Dried stem bark material of *A. julibrissin* was purchased from a drug store in Seoul and identified by Prof. H.J. Chi of this Institute. A voucher specimen is deposited in the herbarium of the Institute.

ISOLATION OF SAPOGENIN.—The powdered stem bark (8 kg) was refluxed with MeOH. The MeOH extract (1.1 kg) was partitioned with hexane (132 g), $CHCl_3$ (173 g), EtOAc (25 g), and *n*-BuOH (320 g), successively. The BuOH soluble portion was hydrolyzed with 5% H_2SO_4 in 50% dioxane for 5 h. The solution was concentrated to a half *in vacuo* and added to crushed ice. The precipitate was filtered, washed with H_2O, dried and subjected to chromatography over silica gel column. The solvent was progressively changed to increasingly polar mixtures of MeOH-$CHCl_3$, and finally to 3% MeOH in $CHCl_3$. Rechromatography of the fraction containing **1**, on elution with C_6H_6-Et_2O (4:1), furnished pure **1** which was crystallized from MeOH-$CHCl_3$ as amorphous white powder (130 mg), mp 258-262°; $[\alpha]^{20}D$ +82.3° (c 0.2, dioxane); uv λ max (MeOH) 215 nm (log ε 4.02); ir ν max (KBr) 3460(OH), 1703, 1650 (C=O and C=C of α,β-unsaturated ester), and 813 cm^{-1} (trisubsituted double bond); ms *m/z* (%) 636 (M^+, 0.5), 618 (M^+-H_2O, 0.9), 590 [M^+-(COOH+H), 0.7], 454 (M^+-TFA, 28.3), 436 [M^+-(TFA+H_2O), 6.3], 428 (**a**, tr.), 409 [M^+-(TFA+COOH), 31.8], 408 [M^+-(TFA+COOH+H), 49.0], 246 (**a**-TFA, 100), 233 (24.0), 207 (**b**, 30.8), 201 [**a**-(TFA+COOH), 80.4], 189 (**b**-H_2O, 28.8), 187 [233-(COOH+H), 24.8].

METHYLATION OF **1**.—The crude sample of **1** (20 mg) was methylated with etherial CH_2N_2, chromatographed over silica gel eluting with C_6H_6 and crystallized from MeOH to yield **2** as fine needles, mp 139-141°; $[\alpha]^{15}D$ +97.3° (c 0.3, $CHCl_3$); ir ν max (KBr) 3420 (OH), 1723 (COOMe), 1710, and 1660 cm^{-1} (C=O and C=C of α,β-unsaturated ester); ms *m/z* (%) 650 (M^+, 0.1), 468 (M^+-TFA, 9.5), 450 [M^+-TFA+H_2O), 1.2], 442 (a, 0.1), 409 [M^+-

(TFA+COOMe), 4.6], 408 [M^+-(TFA+COOMe+H), 9.0], 260 (**a**-TFA, 10.4), 247 (19.6), 207 (**b**, 20.0), 201 [**a**-(TFA+COOMe), 100], 189 (**b**-H_2O, 20.0), 187 [247-(COOMe+H), 34.8].

ACETYLATION OF **2**.—A sample of **2** (10 mg) was acetylated with Ac_2O-pyridine (0.5 ml each) at room temperature overnight. The reaction mixture was evaporated with N_2 gas to remove solvents and crystallized from MeOH-$CHCl_3$ to afford **3** as needles, mp 219-222°; $[\alpha]^{16}D$ +88° (c 0.5, $CHCl_3$); ir ν max (KBr) 1734, 1242 (acetate), 1720 (COOMe), 1710, and 1654 cm^{-1} (α,β-unsaturated ester); pmr ($CDCl_3$) ζ 0.71 (3H, s, Me), 0.85 (6H, s, 2 x Me), 0.92 (3H, s, Me), 1.00 (3H, s, Me), 1.12 (3H, s, Me), 1.27 (3H, s, Me), 1.61 (3H, d, J=6 Hz, β'-Me), 1.65 (3H, s, α-Me), 2.03 (3H, s, MeCO), 2.31 (2H, m, furan H-3), 3.59 (3H, s, OMe), 3.71 (1H, m, furan H-2), 4.35 (2H, m, furan H-5), 4.46 (1H, t, J=7 Hz, H-3), 4.76 (1H, dd, J=6 and 11 Hz, H-21), 5.14 (1H, q, J=6 Hz, H-α'), 5.32 (1H, m, H-12), 6.95 (1H, m, H-β); ms *m/z* (%) 692 (M^+, 0.1), 632 (M^+-HOAc, 0.1), 510 (M^+-TFA, 7.8), 451 [M^+-(TFA+COOMe), 7.9], 450 [M^+-(TFA+COOMe+H), 14.6], 442 (**a**, 0.4), 260 (**a**-TFA, 65.4), 249 (**b**, 5.8), 247 (100), 201 [**a**-(TFA+COOMe), 100], 189 (**b**-HOAc, 22.6), 187 [247-(COOMe+H), 29.2].

SAPONIFICATION OF **1**.—A sample of **1** (30 mg) was refluxed with 5% alcoholic KOH (10 ml) for 4 h. The reaction mixture was concentrated to a half *in vacuo*, added to crushed ice, and acidified with dilute HCl. The precipitate was filtered and crystallized from MeOH to afford 16 mg of compound as plates, mp 306°; $[\alpha]^{16}D$ +83.5° (c 0.1, MeOH), which was identified as machaerinic acid by direct comparison with authentic sample (3) (co-tlc, mmp, and ir). The filtrate was saturated with NaCl and then partitioned with Et_2O. The Et_2O layer was dried over Na_2SO_4 and concentrated. The concentrate was crystallized from MeOH to give 6 mg of compound as plates, mp 118-120°; $[\alpha]^{20}D$ −3° (c 0.3, dioxane), which was identified as 4-(ethylidene)-2-tetrahydrofuranmethacrylic acid by direct comparison with an authentic sample (3) (co-tlc, mmp, ir, uv, and ms).

ACKNOWLEDGMENTS

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