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Sapogenins from *Albizzia julibrissin*

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Abstract □ From the stem bark of *Albizzia julibrissin* (Leguminosae) two known sapogenins, acacigenin B, and machaerinic acid lactone, were isolated and identified by chemical and spectral data. It is the second time that the former was isolated from the plant sources.

Keywords □ *Albizzia julibrissin*, Leguminosae, Acacigenin B, Machaerinic acid lactone.

In the previous communications[1], we reported the isolation of acacic acid lactone and machaerinic acid methyl ester from the stem bark of *Albizzia julibrissin* (Leguminosae). We herein wish to describe the isolation and structure elucidation of further sapogenins from the same source.

The sapogenin mixture, on chromatographic separation, afforded two further sapogenins, named C and D, tentatively.

Compound C(**1**), mp 278-81°, $[\alpha]_D^{20}$+56.7°, showed positive Liebermann-Burchard and tetranitromethane tests and UV absorption maximum at 212 nm (log ε 4.19) indicating the presence of an α,β-unsaturated ester function[2]. This was further corroborated by its IR which showed peaks at 1,700cm^{-1}, 1,650cm^{-1} (C=O and C=C of an α,β-unsaturated ester function) and 3,480cm^{-1} (OH).

On saponification under reflux with alcoholic KOH, **1** furnished acacic acid (**2**), mp 292-3°, which was identfied by direct comparison with an authentic sample[1] and an acid (**3**), mp 118-20°.

The acid(**3**) showed also α,β unsaturated acid function in its IR (1,665 and 1,645cm^{-1}) and UV(215nm, log ε 3.98).

Its NMR showed two methyls at δ 1.60 (3H, d, J=6Hz, H-β') and 1.64(3H, s, H-α CH_3), one α,β unsaturated methylene at 2.25 (2H, m, H-3), one oxymethine proton at 3.80 (1H, dd, J=5 and 8Hz, H-2), one α,β-unsaturated oxymethylene at 4.38 (2H, ABq, J=16Hz, H-5, which further split by long range coupling), two olefinic protons at 5.50 (1H, q-like, J=6Hz, H-α') and 7.10 (1H, m, H-β) and a COOH protcn at 11.0ppm. These spectral data suggested that **3** was β(4-ethylidene)-2-tetrahydrofuran methacrylic acid.

This assumption was further supported by MS of **3** (see Experimental Methods). The compound C(**1**) on treatment with CH_2N_2 yielded a methyl ester (**4**), mp 189-92°, which on acetylation with Ac_2O/pyridine at rcom temperature gave a monoacetate methylester (**5**), mp 171-2°.

The monoacetate formation indicated that C-16 hydroxyl was not esterified with **3**. This result together with the failture of lactonization of **1** during acid treatment strongly suggested that **3** was linked to the hydroxyl group at C-21 in **2**.

MS of **1** was in complete agreement with the above suggestion. It showed an ion peak at *m/z* 634 in the high mass region which corresponded to the loss of one molecule of water from

the molecular ion. Further loss of H_2O and H_2O+CO_2 from the m/z 634 ion resulted in peaks at m/z 616 and 572, respectively.

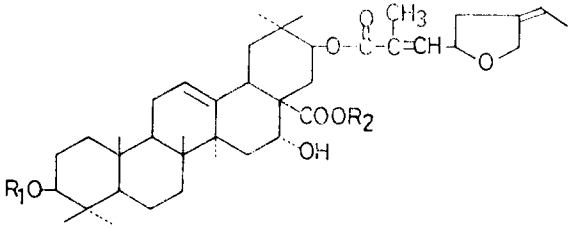
Elimination of 3 from the molecular ion led to the fragment at m/z 470 which again lost one molecule each of water and COOH, respectively, showing peaks at m/z 452 and 425. Subsequent loss of H_2O+CO_2 and $2H_2O+CO_2$ from the m/z 470 fragment gave peaks at m/z 408 and 390, respectively. The fragment ion of m/z 470 underwent a typical retro Diels-Alder fragmentation to furnish peaks at m/z 262 (D/E ring) and 207 (A/B ring)[3]. Elimination of water from the m/z 262 ion produced a fragment at m/z 244 which by loss of COOH gave rise to an ion at m/z 199.

Therefore, **1** was established as acacigenin B which was first isolated from *Acacia concinna*[4].

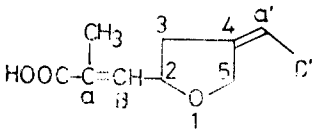
Compound D(**6**), mp 240°, $[\alpha]_D^{20}$ +14.75°, gave also positive result in Liebermann-Burchard test. Its IR showed absorption peaks at 3350(OH), 1760 (γ-lactone), 1630 and 800cm^{-1} (tri-substituted double bond) which was highly reminiscent of that of acacic acid lactone[1].

The NMR showed seven tertiary methyl signals at δ 0.74~1.08 and a signal at 3.20 (1H, t, J=7.5Hz), assigned to C 3 axial proton. The signal at δ 4.10 (d, J=6Hz) was assigned to the lactonic proton and an olefinic proton appeared at δ 5.55 as a multiplet.

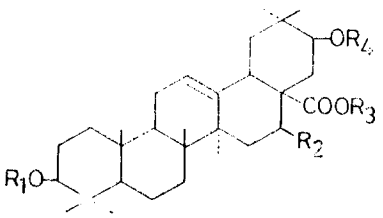
The MS had the molecular ion at m/z 454 and the ions at m/z 246(D/E ring), 207(A/B



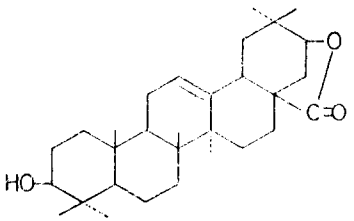
1 $R_1 = R_2 = H$
4 $R_1 = H$ $R_2 = Me$
5 $R_1 = Ac$ $R_2 = Me$



3



2 $R_1 = R_3 = R_4 = H$ $R_2 = \alpha$-OH
7 $R_1 = R_3 = R_4 = H$ $R_2 = H$
8 $R_1 = R_2 = R_4 = H$ $R_3 = Me$
9 $R_1 = R_4 = Ac$ $R_2 = H$ $R_3 = Me$



C

ring) and 201(246-COOH). All the spectral data coincided with the reported ones for sapogenin B[5].

Furthermore, treatment of compound D(**6**) with alkali furnished machaerinic acid(**7**), mp 306°, which on methylation with CH_2N_2 followed by acetylation with Ac_2O/pyridine gave machaerinic acid methylester(**8**), mp 222-4°, and diacetyl machaerinic acid methyl ester(**9**), mp 225-30°, respectively. All the derivatives were identified by direct comparisons with authentic samples.

From the above results, the compound D was identified as machaerinic acid lactone (=sapogenin B).

EXPERIMENTAL METHODS

The mps were taken on a Mitamura-Riken apparatus and are uncorrected. NMR spectra were measured at 80MHz in $CDCl_3$ solution with TMS as internal standard and MS spectra were recorded with a direct inlet system at 70eV.

Isolation of Sapogenins

The MeOH extract of the stem bark of *A. julibrissin* was worked up as described in the preceeding paper[1].

Compound C (**1**)

Crystallized from MeOH as whitish amorphous powder, mp 278-81°, $[\alpha]_D^{20}$ +56.7 (C=0.41, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1700, 1656 (C=O and C=C of α,β-unsaturated ester); UV λ_{max}^{EtOH} nm (log ε): 212 (4.19); NMR (DMSO-d_6, TMS): δ 0.66~1.55 (9 x Me), 2.18(2H, m, furan H-3), 3.75(3H, m, H-3, H-16, furan H-2), 4.23(2H, m, furan H-5), 4.90(1H, m, H-21), 5.20(1H, m, H-12), 5.40(1H, m, α'-H), 6.88(1H, m, β-H).

Compound D (**6**)

Crystallized from MeOH as needles, mp 240°, $[\alpha]_D^{20}$ +14.75 (C=0.122, MeOH); IR ν_{max}^{KBr}cm^{-1}: 3350 (OH), 1760 (γ-lactone), 1630, 800 (trisubstituted double bond).

Saponification of **1**

A sample of **1** (50mg) was refluxed with 4% alcoholic KOH (15ml) for 4hr. The reaction mixture was concentrated to a half, added to crushed ice and acidified with d-HCl. The precipitate was filtered and crystallized from MeOH to afford **2** as needles, mp 292-3°, which was identified by direct comparison with an authentic sample (TLC, mmp and IR).

The filtrate was saturated with NaCl and then extracted with ether. The ether layer was dried over Na_2SO_4 and concentrated. The concentrate was crystallized from MeOH to give **3** as plates, mp 118-20, $[\alpha]_D^{20}$ -3° (C=0.3, dioxane); IR ν_{max}^{KBr} cm^{-1}: 1665, 1645 (C=O and C=C of α,β-unsaturated acid), 1378 (CH_3), 1110, 1050 (cyclic ether), 840, 815 (trisubstituted double bond); UV λ_{max}^{MeOH} nm (log ε): 215 (3.98); MS *m/z* (%): 182 (M^+, 54.2), 167 ($M^+ - CH_3$, 15.8), 97 (11.0), 85 (100), 69 (63.4), 41(44.4).

Methylation of **1**

A sample of **1** (50mg) was methylated with etherial CH_2N_2 and crystallized from MeOH to yield **4** as amorphous white, mp 189-92°, IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1720-1700, 1600 (C=O and C=C of α,β unsaturated ester).

Acetylation of **4**

A sample of **4** (40mg) was acetylated with Ac_2O and pyridine(1ml each) at room temperature overnight. The reaction mixture was added to crushed ice, filtered and crystallized from MeOH to yield **5** as amorphous powder, mp 171-2°, IR ν_{max}^{KBr} cm^{-1}; 3460 (OH), 1740, 1250 (acetate), 1725-1700, 1660 (C=O and

C—C of α,β unsaturated ester); NMR ($CDCl_3$, TMS): δ 0.70-1.37(7×Me), 1.61(3H, d, J=5.5Hz, H-β'), 1.66(3H, s, α CH_3), 2.01 (3H, s, CH_3CO), 3.59 (3H, s, CH_3O), 3.84(1H, m, furan H-2), 4.10(1H, m, H-16), 4.12(2H, m, furan H-5), 4.50(1H, m, H-3), 5.25-5.65(3H, m, H-12, H-21, H-α'), 7.00(1H, m, H-β).

Saponification of **6**

A sample of **6** (10mg) was refluxed with 5% alcoholic KOH(10ml) for 4hr and followed by the usual work-up. It was crystallized from MeOH to afforded **7** as plates, mp 306°, which was identified as machaerinic acid by direct comparison with an authentic sample (TLC, mmp and IR).

Methylation of **7**

A sample of **7**(10mg) was methylated with CH_2N_2 and crystallized from MeOH to give a methylester (**8**) as needles, mp 222-4°, which was identified by direct comparison with an authentic sample of machaerinic acid methylester (**8**) (TLC, mmp and IR).

Acetylation of **8**

To a sample of **8** (15mg), Ac_2O and pyridine (0.5ml each) were added and allowed to stand at room temperature overnight. The reaction mixture was worked up in the usual manner and crystallized from MeOH to give **9** as needles, mp 225 30°, which was identified by direct comparison with an authentic sample of diacetyl machaerinic acid methyl ester (mmp and TLC).

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