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Studies on Tannins of the Bark of Macaranga tanarius (L.)Muell. Et Arg

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血桐樹皮部單寧成分之研究

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摘　要

血桐[*Macaranga tanarius* (L.) Muell. et Arg. (Euphorbiaceae)]樹皮以含水丙酮冷浸抽取，分離10種單寧成分，分別爲corilagin(1), mallotinic acid(2), geraniin(3), macarinin A(4), putranjivain B(5), putranjivain A(6), mallotunin(7), mallophilinin(8), repandusinic acid A(9) 及phyllanthusiin C(10).各化合物之構造係以其物理化學性質及核磁共振光譜等數據推定之，並與文獻記載數據或標準品直接比對而確認之。

前　言

大戟科(Euphorbiaceae)植物血桐[*Macaranga tanarius* (L.) Muell. et Arg.]爲民間藥，樹皮煎服治痢疾，樹皮及葉研爲末充作醱酵工業之防腐劑，根則爲發燒時之催吐劑，煎服治咳血。[1]

在植物單寧(Tannin)成分研究系列中，有關大戟科植物血桐及蘭嶼血桐[*M. sinensis* (Baill). Muell.-Arg.]之研究，曾提出由血桐葉部分離得23種單寧成分[2]，由蘭嶼血桐葉部分離得18種單寧成分[3]之報告，此次由血桐之樹皮部分離得10種單寧成分，本報告說明其成分分離及構造之決定。

材料與方法

一、材料

血桐樹皮(1987年2月採集自台北近郊)。

二、儀器

本實驗中融點測定使用Yanagimoto micro-melting point apparatus,融點未校正。旋光度以JASCO DIP-4旋光計測定。核磁共振(^{1}H-NMR)光譜儀使用JEOL FX100, JEOL GX270 spectrometer,以TMS爲內標準。Fast atom bombardment mass spectra(FAB-MS)以JEOL JMS-HX 100 mass spectrometer測定。

三、管柱層析使用之膠質

Sephadex LH-20 (25-100μ, Pharmacia Fine Chemical Co., LtD), MCI-gel CHP 20P (75-150μ, Mitsubishi Chemical Industris Co., Ltd), Fuji-gel ODS G3 (43-65μ, Fuji gel Hambai Co., Ltd), Bondapak C_{18}/Porasil B (37-75μ, Waters Associates, Inc.)。

四、抽取及分離

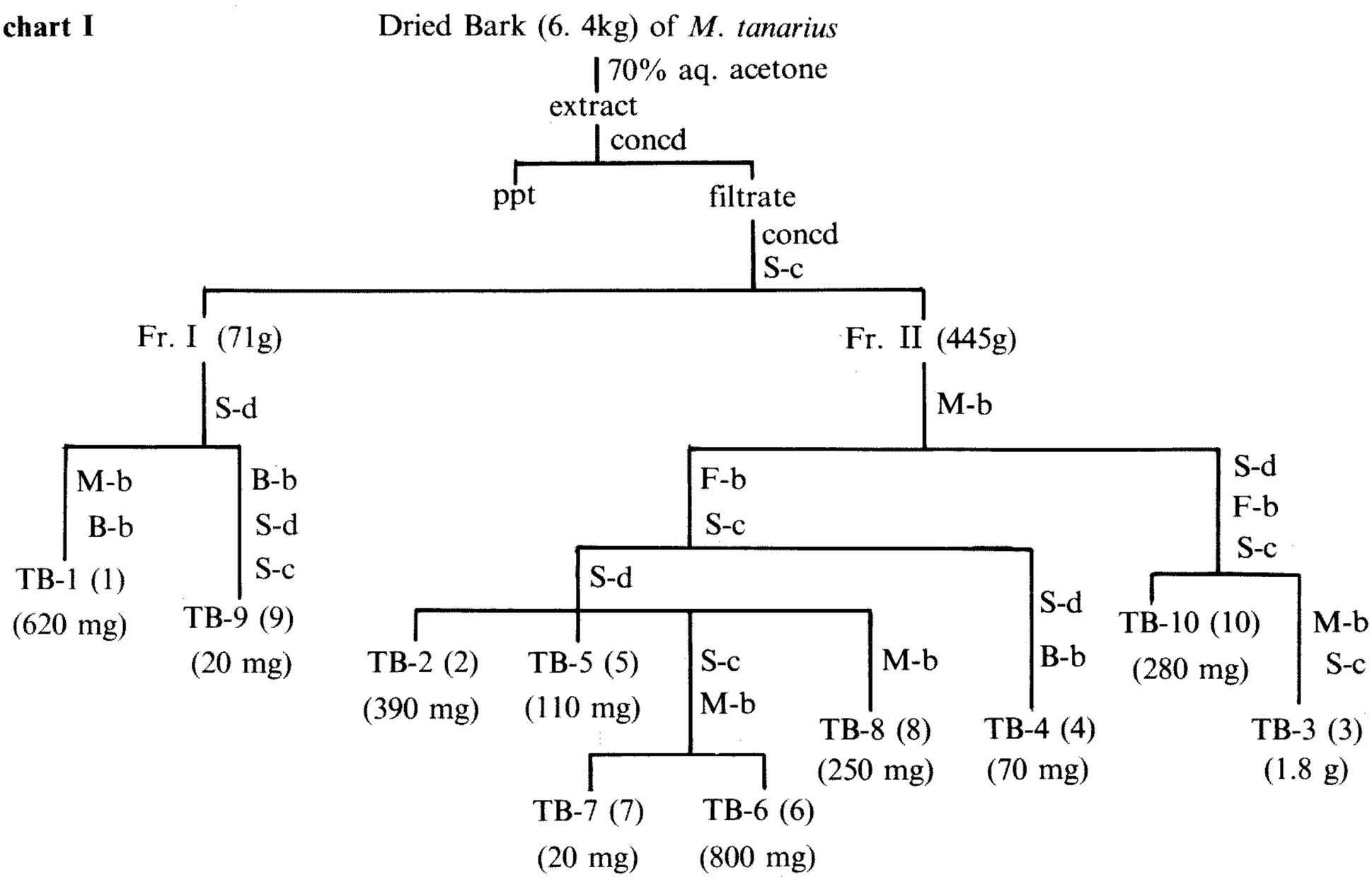
血桐樹皮(6.4Kg)，用70%丙酮室溫下浸泡抽取，抽出液於減壓下將丙酮除去，將析出之沈澱濾去後，濾液利用Sephadex LH-20管柱層析，以H_2O-MeOH-acetone沖提，劃分成Fr.I, Fr.II二部分，如Chart I所示，各部分利用各種管柱層析分離得10種化合物(TB-1～TB-10)。

結果與討論

一、結果

如Chart I所示，利用各種管柱層析分離得10種化合物(TB-1～TB-10)。各化合物之性質及光譜數據如下：

chart I



S: Sephadex LH-20
M: MCI-gel CHP 20P
F: Fuji-gel ODS G-3
B: Bondapak C_{18} / Porasil B

a: H_2O-MeOH-acetone
b: H_2O-MeOH
c: 80% MeOH
d: EtOH

TB-1: ***Corilagin*** *(1)*

白色無晶形粉末，$[\alpha]_D^{21}$-190.2° (c＝0.8, acetone). ^{1}H-NMR (acetone-d_6)δ: 4.01-4.20 (2H, m, H-2,6), 4.43-4.64(2H, m, H-4,5), 4.83-5.08 (2H, m, H-3,6), 6.38(1H, s, H-1), 6.69, 6.84 [each 1H, s, hexahydroxydiphenoyl (HHDP)-H], 7.12 (2H,s, galloyl H).

TB-2: ***Mallotinic acid*** *(2)*

淡褐色無晶形粉末，$[\alpha]_D^{23}$-75.7° (c＝0.9, MeOH). ^{1}H-NMR (acetone-d_6)δ: 3.99 (1H, broad [br] s, H-2), 4.08 (1H, dd, J＝7, 10Hz, H-6),4.42 (1H, brs, H-4), 4.49 (1H, br t, J＝ 10Hz, H-5), 4.71 (1H, t, J＝10Hz, H-6), 4.75 (1H, br s ,H-3), 6.33 (1H, d, J＝3Hz, H-1), 6.64, 6.72, 7.13 (each 1H, s, valoneayl H), 7.19 (2H, s, galloyl H).

TB-3: ***Geraniin*** *(3)*

黃色粉末(H_2O), mp 218-221°C (dec.), $[\alpha]_D^{22}$-147.8° (c＝0.9, MeOH). ^{1}H-NMR (acetone-d_6＋D_2O)δ: 4.28-4.50 (1H, m, H-6), 4.68-4.85 (2H in total, H-5,6), 4.89 [1/4H, br s, dehydrohexahydroxydiphenoyl (DHHDP) H-1], 5.15 (3/4H, s, DHHDP H-1), 5.35-5.46 (3H in total, H-2,3,4), 6.20 (1/4H, br s, DHHDP H-3), 6.48 (3/4H, s, DHHDP H-3), 6.55 (1H, s, H-1), 6.63, 7.05 (each 1H, s, HHDP H), 7.17 (2H,s, galloyl H), 7.23 (1 H, s, DHHDP H-3').

TB-4: ***Macarinin A*** *(4)*

淡黃色無晶形粉末，$[\alpha]_D^{15}$-42.0° (c＝1.1, MeOH). ^{1}H-NMR (acetone-d_6＋D_2O)δ: 4.25-4.50 (1H, m, H-6), 4.60-4.90 (2H, m, H-5,6), 4.94 (1/3 H, d, J＝2Hz, DHHDP H-1), 5.17 (2/3H, s, DHHDP H-1), 5.35-5.60 (3H, m, H-2,3,4), 6.25 (1/3H, d, J＝2Hz, DHHDP H-3),6.53 (2/3H, s, DHHDP H-3), 6.54 (1H, br s, H-1), 6.73, 7.01, 7.11,7.19,7.20,7.26 (4H in total, each s, aromatic H), 7.21 (2H,s, galloyl H).

TB-5: ***Putranjivain B*** *(5)*

白色粉末(H_2O), mp 229-230°C. $[\alpha]_D^{23}$-68.6°(c=1.0, acetone). ^{1}H-NMR (acetone-d_6)δ: 1.64 [1H, d, J=14Hz, putranjivainoyl (put.) H-3], 2.78 [1H, br d, J=14Hz, put. H-3], 4.29 (1H, s, put. H-3″), 4.61 (1H, m, H-3), 4.84 (1H, s-like, put. H-1), 4.98 (1H, m, H-4), 5.01 (1H, s, put. H-1″), 5.34 (1H, br d, J=3Hz, H-2), 6.37 (1H, d, J=3Hz, H-1), 7.21 (2H, s, galloyl H), 7.35 (1H, s, put. H-3').

TB-6: ***Putranjivain A*** *(6)*

無色板狀晶(H_2O), mp 252-253°C(dec.). $[\alpha]_D^{24}$-62.0° (c=1.0, MeOH). ^{1}H-NMR (270 MHz, acetone-d_6)δ: 1.64 (1H, d, J=14Hz, put. H-3), 2.72 (1H, dd, J=1.5,14Hz, put. H-3), 3.94(1H, m, put. H-5″), 4.17 (1H, s-like, put. H-4″), 4.19 (1H, m, put. H-5″), 4.25(1H, s, put. H-3″), 4.45 (1H, dd, J=8, 11Hz, H-6), 4.72 (1H, dd, J=9, 11Hz, H-6), 4.75 (1H, d, J=1.5Hz, put. H-1), 4.92 (1H, dd, J=8, 9Hz, H-5), 5.05 (1H, s, put. H-1″), 5.35 (1H, d, J=4Hz, H-3), 5.61 (1H, s, H-2), 5.66 (1H, d, J=4Hz, H-4), 6.53 (1H, s, H-1), 6.66, 7.08 (each 1H, s, HHDPlH), 7.19 (2H, s, galloyl H), 7.32 (1H, s, put. H-3').

TB-7: ***Mallotunin*** *(7)*

淡褐色無晶形粉末，$[\alpha]_D^{23}$-48.3° (c=0.5, MeOH).^{1}H-NMR (acetone-d_6+D_2O)δ: 1.62 (1H, d, J=14Hz, put. H-3), 2.72 (1H, br d, J=14Hz, put. H-3), 4.73 (1H, s-like, put. H-1), 5.03 (1H, s, put. H-1″), 5.33 (1H, br d, J=4Hz, H-3), 5.41(1H, br d, J=2Hz, H-2), 5.57 (1H, br, H-4), 6.46(1H, d, J=2Hz, H-1), 6.67, 6.85, 7.14 (each 1H, s, valoneaylH), 7.25 (2H, s,galloyl H), 7.26 (1H, s, put. H-3').

TB-8: ***Mallophilinin*** *(8)*

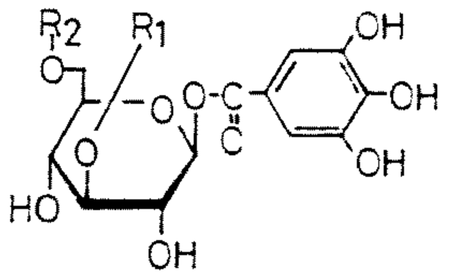
淡褐色無晶形粉末，$[\alpha]_D^{13}$-7.3° (c=1.0, MeOH). ^{1}H-NMR(270MHz, acetone-d_6+D_2O)δ: 1.63 (1H, d, J=14Hz, put. H-3), 2.74(1H, J=14Hz, put. H-3), 4.17(1H, s-like, put. H-4″), 4.23(1H, s, put. H-3″), 4.51 (1H, dd, J=8,10Hz, H-6), 4.74 (1H, s-like, put. H-1), 5.04 (1H, s, put. H-1″), 5.32 (1H, br d, J=4Hz, H-3), 5.62 (1H, br s, H-2), 5.71 (1H, br s, H-4), 6.54 (1H, s, H-1), 6.69, 6.85,7.01 (each 1H, s, tergalloyl H), 7.21 (2H, s, galloyl H), 7.32 (1H, s, put. H-3')

TB-9: ***Repandusinic acid A*** *(9)*

淡褐色無晶形粉末，$[\alpha]_D^{13}$-54.3° (c=0.9, MeOH). ^{1}H-NMR (270 MHz, acetone-d_6)δ: 4.23 (1H, d, J=4Hz, H-2), 4.29 (1H, dd, J=7, 10Hz, H-6), 4.60 (1H, t, J=7Hz, H-5), 4.69 (1H , dd, J=7, 10Hz, H-6), 4.88 (1H, d, J=4Hz, H-3), 5.31 [1H, d, J=2Hz, dehydrochebuloyl(DCHE) H-2), 5.56 (1H, d, J=2Hz, DCHE H-3), 5.60(1H, d, J=4Hz, H-4), 6.23 (1H, d, J=4Hz, H-1), 6.70, 6.85 (each 1H, s, HHDP H), 7.13 (2H, s, DCHE H-3',5), 7.15 (2H, s, galloyl H).

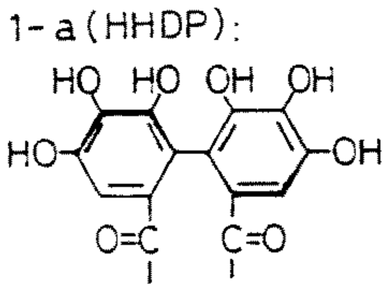
TB-10: ***Phyllanthusiin*** *C(10)*

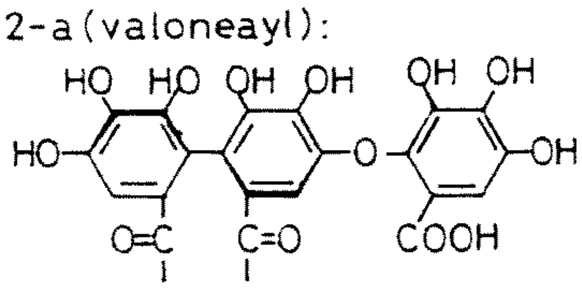
淡褐色無晶形粉末，$[\alpha]_D^{19}$-80.3° (c=0.8, MeOH). negative FAB-MS m/z: 633, 925[M-H]$^-$. ^{1}H-NMR (270 MHz, acetone-d_6)δ:2.24(1H, t, J=11Hz, 2,4-acyl H-3), 2.44 (1H, dd, J=7, 11Hz, 2,4-acyl H-3), 4.37 (1H, dd, J=12, 14Hz, H-6), 4.61 (1H, dd, J=7, 11Hz, 2,4-acyl H-4), 4.63 (1H, s, 2,4-acyl H-1), 4.84～4.93 (2H, m, H-5,6), 5.39 (1H, d, J=2Hz, H-4), 5.58 (2H, br s, H-2,3),

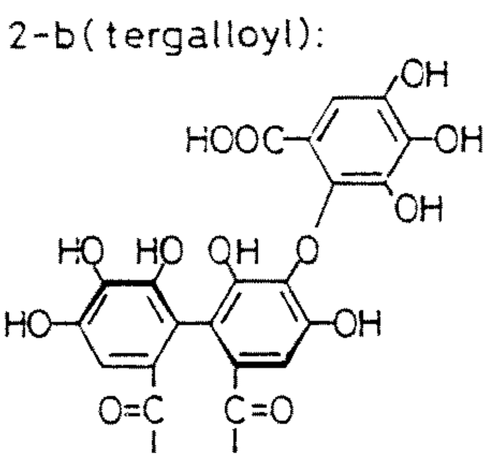


1. R_1,R_2= 1-a

2. R_1,R_2= 2-a







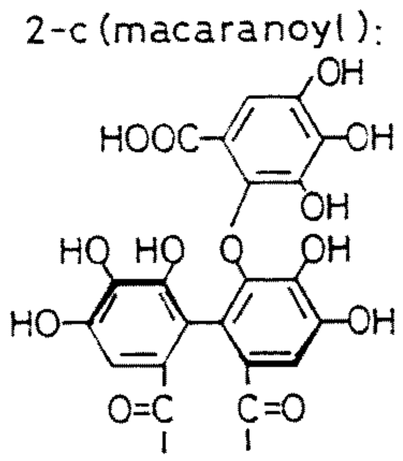


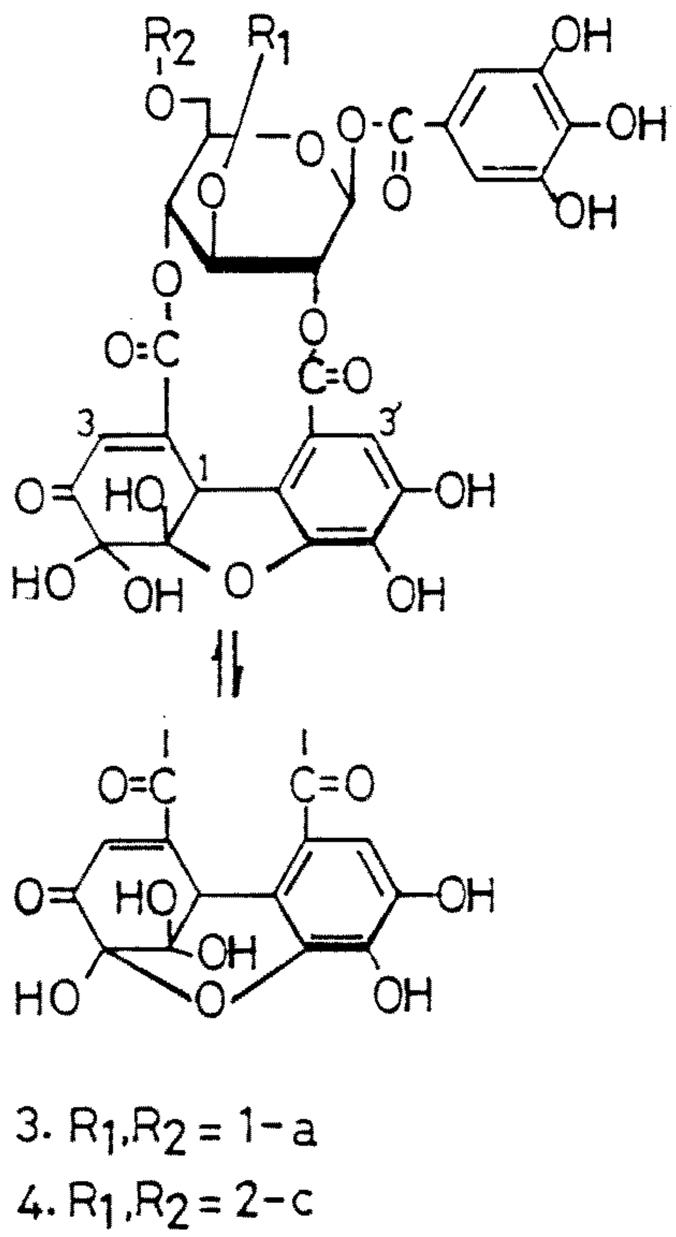
Figure 1. Structures of 1, 2 and 1a, 2a, 2b, 2c

6.40 (1H, s, H-1), 6.68, 7.05 (each 1H, s, HHDP H), 7.10 (2、4-acyl H-3'), 7.15 (2H, s, galloyl H). ^{13}C-NMR(acetone-d_6 + D_2O)δ: 46.3 (t), 65.8 (glc C-4), 63.2(d), 62.5(glc C-3), 63.9 (glc C-6), 68.1 (glc C-2), 72.8 (glc C-5), 74.8(d), 78.3 (s), 92.0(glc C-1), 107.6 (HHDP C-3,3'), 110.6(galloyl C-2, 6), 116.9, 117.2 (HHDP C-1, 1'), 119.9(galloyl C-1), 124.3, 125.4 (HHDP C-2,2'), 136.4, 137.8 (HHDP C-5,5'), 140.0 (galloyl C-4), 144.7, 144.9, 145.2, 145.5 (HHDP C-4,4',6,6'), 145.9 (galloyl C-3,5'), 119.2(2,4-acyl C-1'), 115.4 (2,4-acyl C-2'), 111.3 (2,4-acyl C-3'), 147.0(2,4-acyl C-4'), 135.8 (2,4-acyl C-5'), 149.7 (2,4-acyl C-6'), 164.8, 165.3, 166.5, 168.9, 173.6 (-COO-).

二、討論

如實驗部分所述，由血桐之樹皮部分離得到之10種單寧類化合物(TB-1～TB-10)，其構造之決定如下：

TB-1爲白色無晶形粉末，$[\alpha]_D$ −190.2°，其^{1}H-NMR光譜顯示之galloyl基[δ 7.12 (2H, s)]，HHDP基[δ 6.69, 6.84 (each 1H, s)]及糖[δ 6.38 (1H, s), anomeric H]之吸收峰與corilagin (1)標準品比較均一致，故而確認TB-1爲corilagin.[2]



3. R_1,R_2 = 1-a
4. R_1,R_2 = 2-c

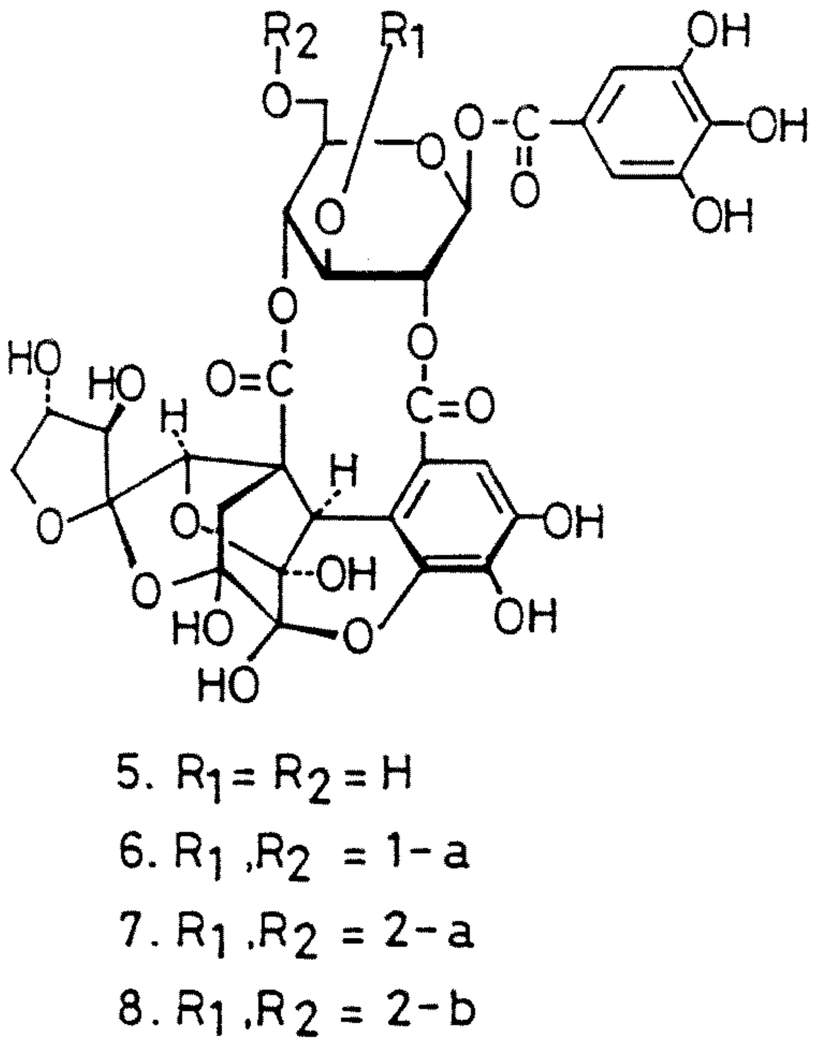
Figure 2. Structures of 3 and 4

TB-2爲淡褐色無晶形粉末，$[\alpha]_D$ −75.7°，其^{1}H-NMR光譜顯示糖之吸收峰與corilagin相類似，亦即glucose之1,3,6位之OH基均醯基化，且在3,6位爲架橋之醯基。在aromatic領域中則呈現1個2H之singlet[δ 7.19 (2H, s)]及3個1H之singlet[δ 6.64, 6.72, 7.13 (each 1H,s)]。因此推測TB-2爲1位接galloyl基，3,6位則可能爲接valoneayl基(2-a)(即mallotinic acid)[4]，tergalloyl基(2-b)(即mallorepanin)[3]或macaranoyl基(2-c)(即macarinin C)[3]之單寧類化合物。經與各化合物直接比較其^{1}H-NMR等而確認TB-2構造爲，3,6位接valoneayl基之mallotinic acid(2)（如圖一）。

TB-3爲黃色結晶性粉末，$[\alpha]_D$ −147。8°，其^{1}H-NMR光譜上呈現DHHDP基之5員環及6員環平衡狀態之特有吸收峰[δ4.89 (1/4H, br s), 5.15 (3/4H, s), 6.20 (1/4H, br s), 6.48 (3/4H,s)]及糖之anomeric H[δ 6.59 (1H, s)]之吸收峰。在aromatic領域，TB-3呈現galloyl基[δ 7.17 (2H,s)]，DHHDP基H-3[δ 7.23 (1H, s)]之吸收峰外，還有在δ 6.63, 7.05 (each 1H, s)之吸收，爲HHDP基之吸收峰，以上之數據顯示TB-3爲1-0-galloyl-2,4-(R)-DHHDP-3,6-(R)-HHDP-β-D-glucopyranose(geraniin)(3) (如圖二)，經與geraniin標準品直接比對而確認之。[2]

TB-4爲黃色無晶形粉末，$[\alpha]_D$ −42.0°，其^{1}H-NMR光譜中aliphatic領域及anomeric H[δ 6.54 (1H, s)]之吸收及DHHDP基平衡狀態之吸收特徵[δ 4.94 (1/3H, d, J＝2Hz), 5.17 (2/3H,s), 6.25 (1/3H, d, J＝2Hz), 6.53 (2/3H, s)]均與TB-3極爲類似，而在aromatic領域之吸收除galloyl基[δ 7.21 (2H, s)]之吸收外，尚有δ 6.73, 7.01, 7.11, 7.19, 7.20, 7.26 (4H in total, each s)共4個aromatic H之吸收，顯示TB-4與TB-3之glucose母核具有相同之conformaton, 爲在1位接有galloyl基，2,4位接有DHHDP基，而3,6位接有galloyl substituted之HHDP基，此可能爲valoneayl基(2-a), tergalloyl基(2-b)或mcaranoyl基(2-c)，經與三者之^{1}H-NMR光譜比對，與3,6位接tergalloyl基之macarinin A(4)[3](如圖二)完全一致，並與標準品直接比較而確認其構造如4。

TB-5爲白色粉末，$[\alpha]_D$ −68.6°，其^{1}H-NMR光譜在δ 1.64, 2.78 (each 1H, d, J＝14Hz)呈現geminal proton之吸收峰，以及在δ 4.29, 4.84, 5.01及7.35 (each 1H,s)之吸收峰與putranjivainoyl基之吸收甚爲類似。在圖譜上又呈現anomeric H之吸收峰[δ 6.37 (1H, d, J＝3Hz)]及galloyl基之吸收峰[δ 7.21 (2H,s)]，由以上數據推定TB-5爲putra-



5. $R_1 = R_2 = H$
6. R_1, R_2 = 1-a
7. R_1, R_2 = 2-a
8. R_1, R_2 = 2-b

Figure 3. Structures of 5,6,7 and 8

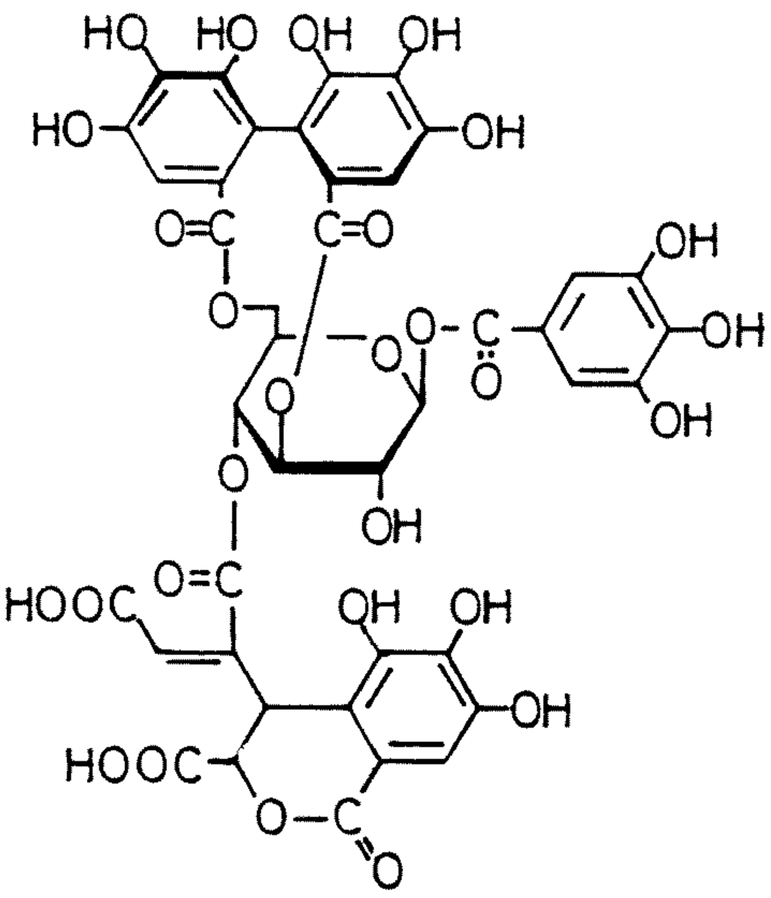


Figure 4. Structures of 9

njivain B(5)[5] 如圖三，經比對其^{1}H-NMR光譜及諸物理數據而確認之。

TB-6爲無色板狀晶，$[\alpha]_D$-62.0°；TB-7爲淡褐色無晶形粉末，$[\alpha]_D$-48.3°；TB-8爲淡褐色無晶形粉末，$[\alpha]_D$-7.3°。三者之^{1}H-NMR光譜如實驗部分所述，均具有由putranjivainoyl基而來之吸收峰及glucose之吸收峰，且glucose之OH基均被醯基化。三者在aromatic領域之吸收則各有不同：在TB-6而言，除galloyl基之吸收及putranjivainoyl基之H-3之吸收外，尚有在δ 6.66, 7.08 (each 1H,s)歸屬爲HHDP基之吸收峰。以上數據經與putranjivain A比較均一致而確認TB-6爲putranjivain A(6).[4]TB-7及TB-8則除galloyl基及putranjivainoyl基之H-3之吸收外，尚有三個1H之singlet吸收[TB-7: δ 6.67, 6.85, 7.14 (each 1H, s); TB-8: δ 6.69, 6.85, 7.01 (each 1H, s)]，顯示TB-7及TB-8均爲glucose之1位接galloyl基，2,4位接有putranjivainoyl基，而3,6位則接有valoneayl基(2-a)，tergalloyl基(2-b)或macaranoyl基(2-c)之單寧類化合物，經直接與mallotunin(7)[6]及mallophilinin(8)[7]比較^{1}H-NMR光譜及諸物理性質而確認TB-7爲3,6位接valoneayl基之mallotunin; TB-8爲3,6位接tergalloyl基之mallophilinin（如圖三）。

TB-9爲淡褐色粉末，$[\alpha]_D$-54.3°，其^{1}H-NMR光譜與neochebulagic acid比較，glucose之pattern極爲類似[δ 6.23 (1H, d, J=4Hz, H-1), 5.60 (1H, d, J=4Hz, H-4), 4.88 (1H, J=4HZ, H-3), 4.69 (1H, dd, J=7, 10Hz, H-6), 4.60 (1H, t, J=7Hz, H-5), 4.29 (1H, dd, J=7,10Hz, H-6), 4.27 (1H, d, J=4Hz, H-2)]，顯示glucose之1,3,4,6位之OH基均被醯基化，此外^{1}H-NMR光譜亦呈現有galloyl基[δ 7.15 (2H, s)]及HHDP基[δ 6.70 6.85 (each 1H, s)]，故可能爲1-0-galloyl-3,6-HHDP-4-acyl-glucopyranose。由於neochebulagic acid之chebuloyl基之吸收在TB-9均未呈現，代之於δ 7.13[2H, s, dehydrochebuloyl(DCHE) H-3, 5], 5.56, 5.31 (each 1H, d, J=2Hz, DCHE H-2,3)呈現吸收峰，因此推測爲glucose之4位爲接4-dehydrochebuloyl基之repandusinic acid A,[8]經直接比對其諸物理數據及^{1}H-NMR光譜均完全一致而確認TB-9爲repandusinic acid A(9)（如圖四）。

TB-10爲淡褐色無晶形粉末，$[\alpha]_D$-80.3°，^{1}H-NMR光譜呈現galloyl基[δ 7.15 (2H, s)]，HHDP基[δ 6.68, 7.05 (each 1H, s)]及由糖而來之訊號；由糖而來之訊號皆於δ 4.37-6.40間，較低磁場位置呈現，顯示糖之OH基均被醯基化。此外在δ 2.24(1H, t, J=11Hz), 2.44 (1H, dd, J=7,11Hz)及δ 4.61 (1H, dd, J=7,11Hz)呈現ABX型吸收峰，在δ4.83 (1H, s)呈現一個benzylmethine H之singlet；在δ7.10 (1H, s)則呈現一個aromatic H之singlet吸收。

TB-10之negative FAB-MS圖譜在m/z 925顯示$[M-H]^-$之尖峰，又在m/z 633出現相當於corilagin (1)之$[M-H]^-$之尖峰。

就TB-10之^{13}C-NMR光譜檢討，除了galloyl基，HHDP基及glucose之吸收訊號外，在δ46.3(t)呈現methylene;在δ63.2(d)及74.8(d)爲methine;在δ78

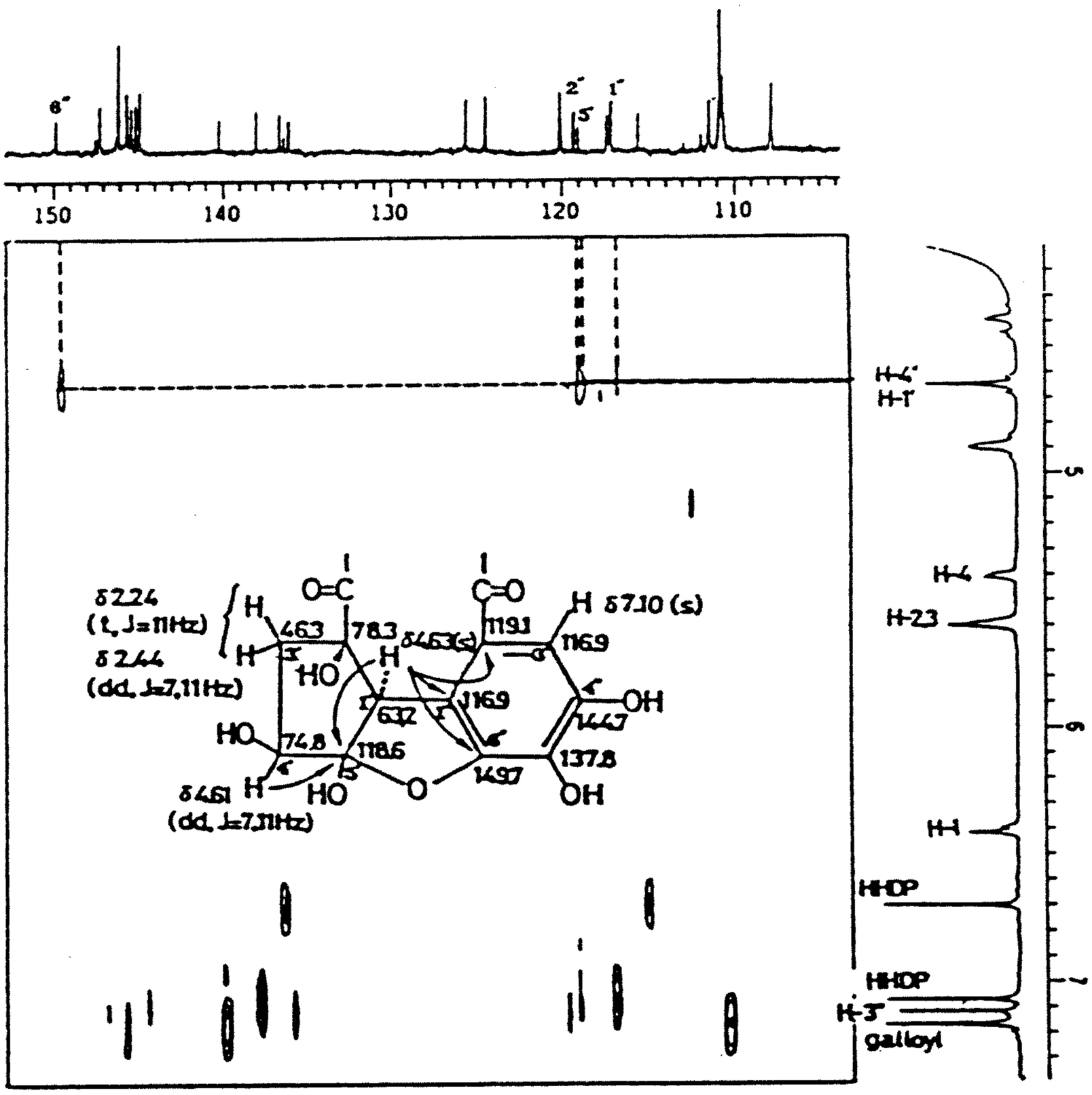


Figure 5. ^{1}H-^{13}C Long-Range COSY Specturm of 10 (in acetone-d_6, Jch=8Hz)

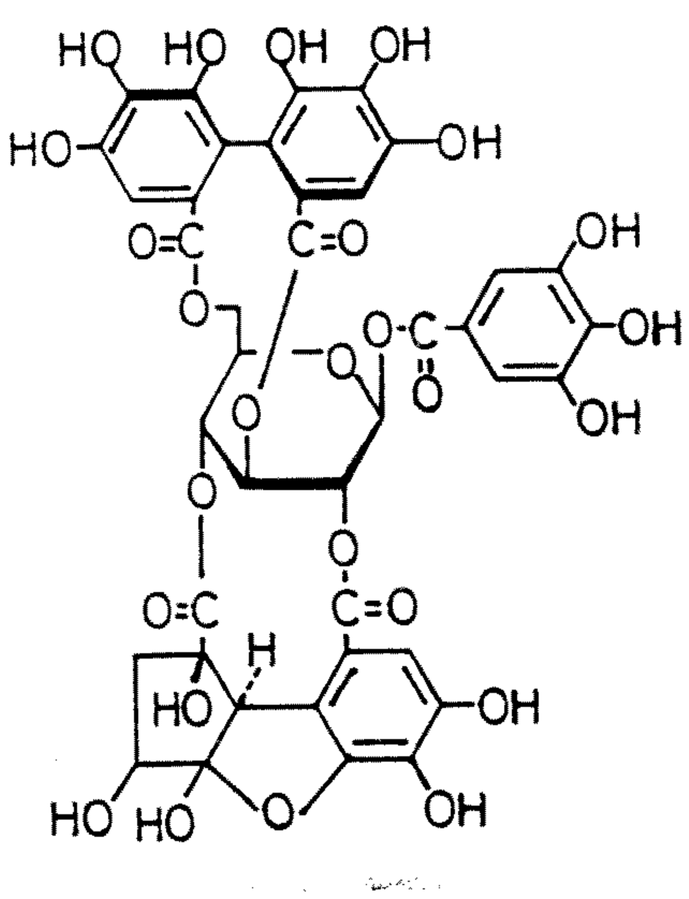


Figure 6. Structures of 10

.3(s)則爲四級碳之吸收訊號；此外，在δ116.9(s, C-1″), 119.2 (s, C-2″), 116.9 (d, C-3″), 144.9 (s, C-4″), 135.8 (s, C-5″), 149.7 (s, C-6″)之訊號與DHHDP基之5員環hemiacetal構造之芳香環部分之訊號極爲類似。δ118.6之訊號依^{1}H-^{13}C long-range COSY光譜(如圖五)所示，與δ4.61,及4.63之methine H具cross peak,可知爲四級碳。綜合以上^{1}H-NMR圖譜，^{13}C-NMR圖譜及negative FAB-MS推測TB-10之構造如10。經查文獻記載phyllanthusiin C之數據，[9]兩者完全一致，故而確認其爲phyllanthusiin C(10)(如圖六)。

血桐樹皮部所含單寧成分與葉部同樣以geraniin(3)爲主成分；樹皮部所分離出之單寧皆以glucose爲母核之加水分解型單寧，且glucose之conformation皆爲$^{1}C_4$-(或skew boat)型，而2,4位及3,6位結合多樣之醯基(valoneayl基, tergalloyl基, DHHDP基及putranjivainoyl基)爲其特徵。再者，葉部含有之多種gallotannin在樹皮部均未被分離

得到。顯示同植物之不同部位所含之成分仍有極大之差異。

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考參文獻

1. 甘偉松.1965.臺灣藥用植物誌.第三卷.p.433.國立中國醫藥研究所.台北縣.
2. Lin, J. H., Nonaka, G., Nishioka, I. 1990. Tannins and Related Compounds. XCIV. Isolation and Characterization of Seven New Hydrolyzable Tannins from the Leaves of *Macaranga tanarius* (L.) Muell. et Arg. Chem. Pharm. Bull . 38 : 1218.
3. Lin, J. H., Ishimatsu, M., Tanaka, T., Nonaka , G., Nishioka, I.1990. Tannins and Related Compounds. XCVI. Structures of Macaranins, New Hydrolyzable Tannins Possessing Macaranoyl and Tergalloyl Ester Groups, from the Leaves of *Macaranga sinensis* (Baill.) Muell. Arg. Chem. Pharm. Bull. 38 : 1844.
4. Saijo, R., Nonaka, G. and Nishioka, I.1989. Tannins and Related Compounds. LXXXIV. Isolation and Characterization of Five New Hydrolyzable Tannins from the Bark of *Mallotus japonicus*. Chem. Pharm. Bull. 37 : 2624.
5. 石松眞，野中源一郎，西岡五夫.1989.大戟科，連香樹科及苦木科植物中新奇加水分解型單寧putranjivain A及B之構造.日本生藥學會第36回年會(熊本)演講要旨.p.172.
6. 西條玲子，野中源一郎，西岡五夫.1988. *Mallotus*屬植物之單寧及相關化合物(3)—*Mallotus japonicus*樹皮部之研究，日本藥學會第108回年會(廣島)演講要旨.p.277.
7. 西條玲子，野中源一郎，西岡五夫.1989. *Mallotus*屬植物之單寧及相關化合物(5)--4種新加水分解型單寧之構造.日本藥學會第109回年會(名古屋)演講要旨III.p.156.
8. Saijo, R., Nonaka, G. and Nishioka, I.1989. Tannins and Related Compounds. LXXXVII. Isolation and Characterization of Four New Hydrolyzable Tannins from the Leaves of *Mallotus repandus*. Chem. Pharm. Bull. 37 : 2624.
9. Yoshida, T., Itoh, H., Matsunaga, S., Tanaka, R. and Okuda, T.1992. Tannins and Related Polyphenols of Euphorbiaceas IX. Hydrolyzable Tannins with C Glucose Core from *Phyllanthus flexuosus* Muell. Arg. Chem. Pharm. Bull. 40 : 53.

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Studies on Tannins of the Bark of *Macaranga tanarius* (L.) Muell. et Arg.

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ABSTRACT

Chemical examination of the bark of *Macaranga tanarius* (L.) Muell. et Arg. (Euphorbiaceae) has led to the isolation of 10 known tannins(1-10). These tannins are corilagin (1), mallotinic acid(2), geraniin(3), marcarinin A (4), putranjivain B(5), putranjivain A(6), mallotunin(7), mallophilinin (8), repandusinic acid A(9) and phyllanthusiin C(10). These structures were identified on the basis of their physical properties and spectroscopic evidences.

Key words : *Macaranga tanarius*, Euphorbiaceae, Hydrolyzable tannin.