

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,分別為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.]為民間藥,樹皮煎服治痢疾,樹皮及葉研為末充作醱酵工業之防腐劑,根則為發燒時之催吐劑,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(¹H-NMR)光譜儀使用JEOL FX100, JEOL GX270 spectrometer,以TMS為內標準。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 (25-100 μ , Pharmacia Fine Chemical Co., Ltd), MCI-gel CHP 20P (75-150 μ , Mitsubishi Chemical Industries Co., Ltd), Fuji-gel ODS G3 (43-65 μ , Fuji gel Hambai Co., Ltd), Bondapak C₁₈/Porasil B (37-75 μ , Waters Associates, Inc.)。

四、抽取及分離

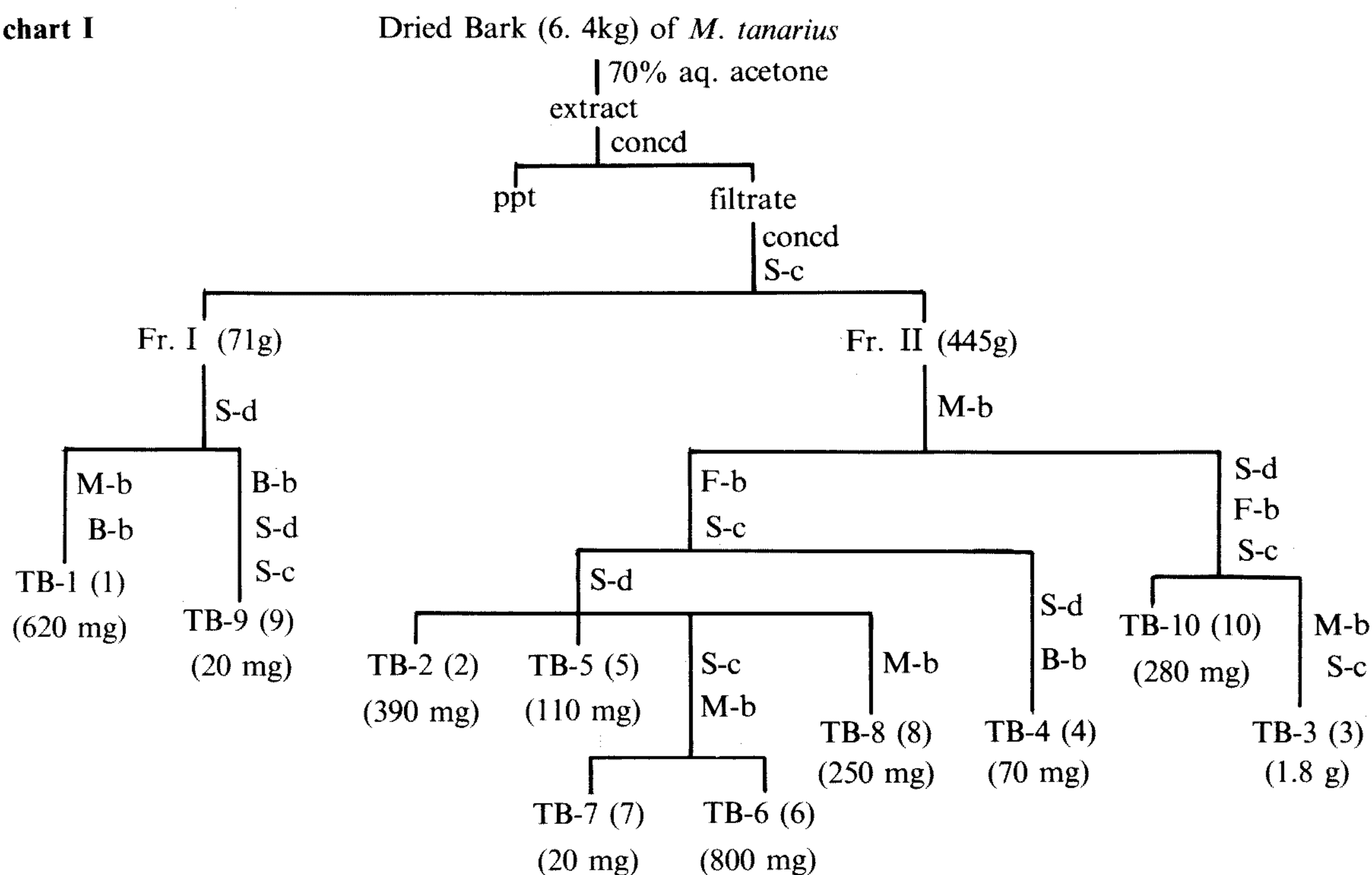
血桐樹皮(6.4Kg),用70%丙酮室溫下浸泡抽取,抽出液於減壓下將丙酮除去,將析出之沈澱濾去後,濾液利用Sephadex LH-20管柱層析,以H₂O-MeOH-acetone沖提,劃分成Fr.I, Fr.II二部分,如Chart I所示,各部分利用各種管柱層析分離得10種化合物(TB-1~TB-10)。

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 C₁₈ / Porasil B

a: H₂O-MeOH-acetone

b: H₂O-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). ¹H-NMR (acetone-d₆)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). ¹H-NMR (acetone-d₆)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 (H₂O), mp 218-221°C (dec.), $[\alpha]_D^{22}$ -147.8° (c=0.9, MeOH). ¹H-NMR (acetone-d₆ +

D₂O)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 (1H, s, DHHDP H-3').

TB-4: *Macarinin A* (4)

淡黃色無晶形粉末, $[\alpha]_D^{25}$ -42.0° (c=1.1, MeOH). ¹H-NMR (acetone-d₆ + D₂O)δ: 4.25-4.50 (1H, m, H-6), 4.60-4.90 (2H, m, H-5,6), 4.94 (1/3H, 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(H₂O), mp 229-230°C. $[\alpha]_D^{23}$ -68.6° (c=1.0, acetone). ¹H-NMR (acetone-d₆)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=3 Hz, 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(H₂O), mp 252-253°C(dec.). $[\alpha]_D^{24}$ -62.0° (c=1.0, MeOH). ¹H-NMR (270 MHz, acetone-d₆)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, 11 Hz, 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, HHDPIH), 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).¹H-NMR (acetone-d₆+D₂O)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, valoneayl H), 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). ¹H-NMR(270MHz, acetone-d₆+D₂O)δ: 1.63 (1H, d, J=14Hz, put. H-3), 2.74(1H, J=14 Hz, 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

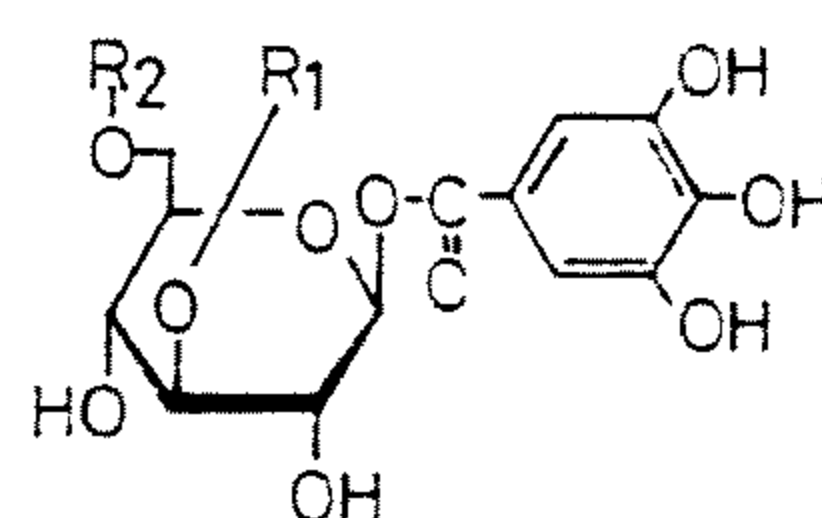
, 6.85,7.01 (each 1H, s, tergalloyl H), 7.21 (2H, s, galloyl H), 7.32 (1H, s, put. H-3')

TB-9: Repandusinic acid A (9)

淡褐色無晶形粉末, $[\alpha]_D^{13}$ -54.3° (c=0.9, MeOH). ¹H-NMR (270 MHz, acetone-d₆)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)

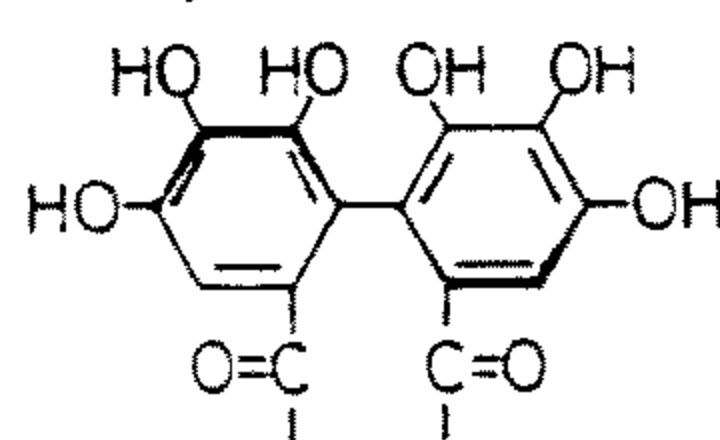
淡褐色無晶形粉末, $[\alpha]_D^{19}$ -80.3° (c=0.8, MeOH). negative FAB-MS m/z: 633, 925[M-H]⁻. ¹H-NMR (270 MHz, acetone-d₆)δ: 2.24(1H, t, J=11Hz, 2,4-acyl H-3), 2.44 (1H, dd, J=7, 11Hz, 2,4-acyl H-3), 4.37 (1H, dd, J=12, 14Hz, H-6), 4.61 (1H, dd, J=7, 11Hz, 2,4-acyl H-4), 4.63 (1H, s, 2,4-acyl H-1), 4.84~4.93 (2H, m, H-5,6), 5.39 (1H, d, J=2Hz, H-4), 5.58 (2H, br s, H-2,3),



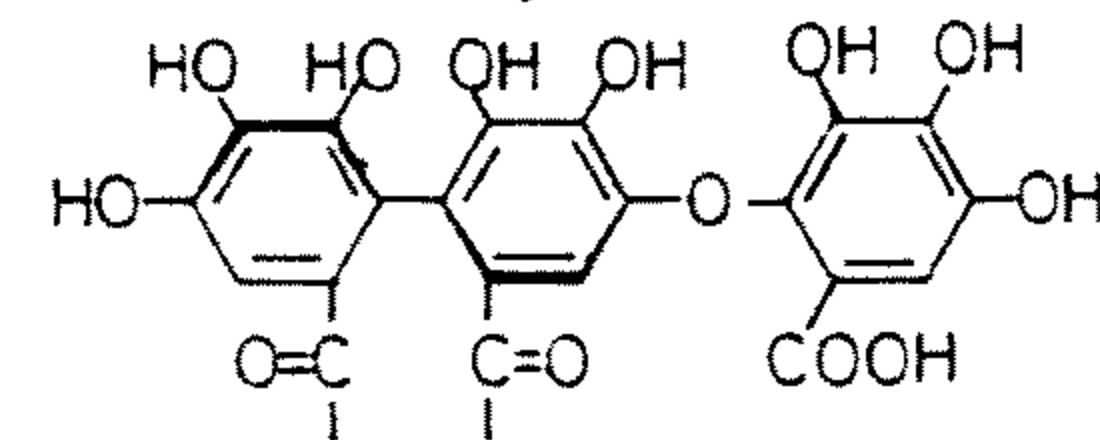
1. R₁,R₂= 1-a

2. R₁,R₂= 2-a

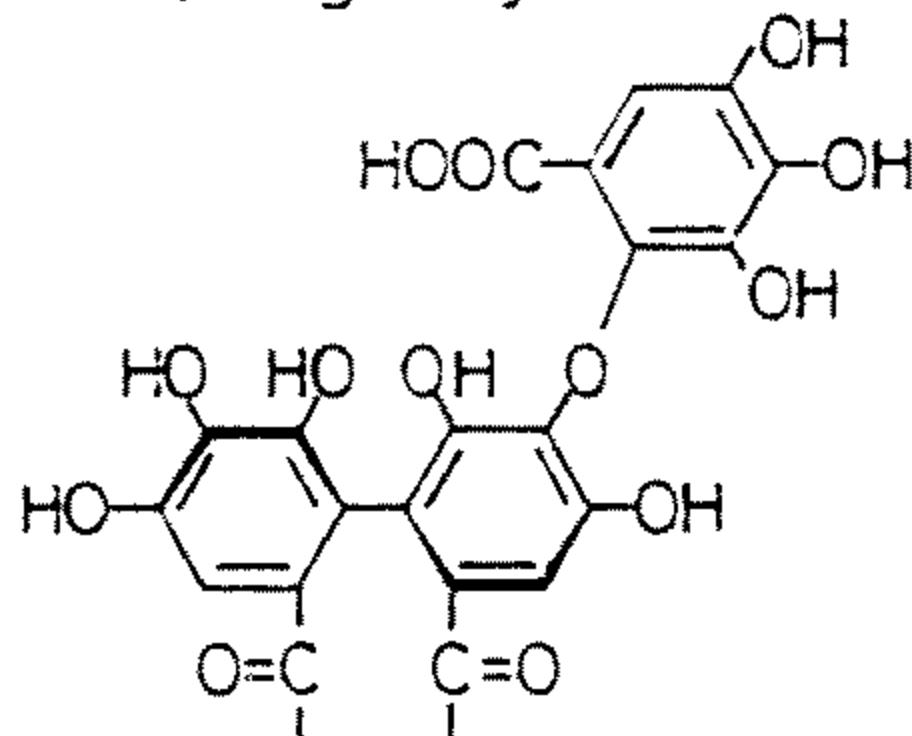
1-a (HHDP):



2-a (valoneayl):



2-b (tergalloyl):



2-c (macaranoyl):

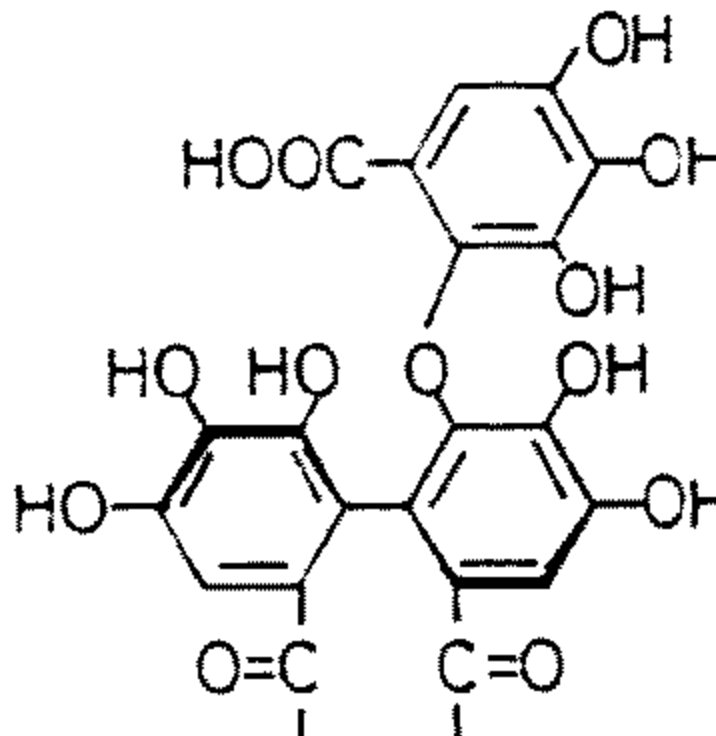


Figure 1. Structures of 1, 2 and 1a, 2a, 2b, 2c

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為白色無晶形粉末, $[\alpha]_D -190.2^\circ$, 其 ^1H -NMR光譜顯示之galloyl基 $[\delta 7.12$ (2H, s)], HHDP基 $[\delta 6.69, 6.84$ (each 1H, s)]及糖 $[\delta 6.38$ (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為corilagin.⁽²⁾

TB-2為淡褐色無晶形粉末, $[\alpha]_D -75.7^\circ$, 其 ^1H -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位為架橋之醯基。在aromatic領域中則呈現1個2H之singlet $[\delta 7.19$ (2H, s)]及3個1H之singlet $[\delta 6.64, 6.72, 7.13$ (each 1H, s)]。因此推測TB-2為1位接galloyl基,3,6位則可能為接valoneayl基(2-a)(即mallotinic acid)⁽⁴⁾, tergalloyl基(2-b)(即mallorepainin)⁽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 ^1H -NMR等而確認TB-2構造為,3,6位接valoneayl基之mallotinic acid(2) (如圖一)。

TB-3為黃色結晶性粉末, $[\alpha]_D -147.8^\circ$, 其 ^1H -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 $[\delta 4.89$ (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 $[\delta 6.59$ (1H, s)]之吸收峰。在aromatic領域, TB-3呈現galloyl基 $[\delta 7.17$ (2H, s)], DHHDP基H-3 $[\delta 7.23$ (1H, s)]之吸收峰外,還有在 $\delta 6.63, 7.05$ (each 1H, s)之吸收,為HHDP基之吸收峰,以上之數據顯示TB-3為1-O-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為黃色無晶形粉末, $[\alpha]_D -42.0^\circ$, 其 ^1H -NMR光譜中aliphatic領域及anomeric H $[\delta 6.54$ (1H, s)]之吸收及DHHDP基平衡狀態之吸收特徵 $[\delta 4.94$ (1/3H, d, $J=2\text{Hz}$), 5.17 (2/3H, s), 6.25 (1/3H, d, $J=2\text{Hz}$), 6.53 (2/3H, s)]均與TB-3極為類似,而在aromatic領域之吸收除galloyl基 $[\delta 7.21$ (2H, s)]之吸收外,尚有 $\delta 6.73, 7.01, 7.11, 7.19, 7.20, 7.26$ (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conformation,為在1位接有galloyl基,2,4位接有DHHDP基,而3,6位接有galloyl substituted之HHDP基,此可能為valoneayl基(2-a), tergalloyl基(2-b)或mcaranoyl基(2-c),經與三者之 ^1H -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為白色粉末, $[\alpha]_D -68.6^\circ$, 其 ^1H -NMR光譜在 $\delta 1.64, 2.78$ (each 1H, d, $J=14\text{Hz}$)呈現geminal proton之吸收峰,以及在 $\delta 4.29, 4.84, 5.01$ 及 7.35 (each 1H, s)之吸收峰與putranjivainoyl基之吸收甚為類似。在圖譜上又呈現anomeric H之吸收峰 $[\delta 6.37$ (1H, d, $J=3\text{Hz}$)]及galloyl基之吸收峰 $[\delta 7.21$ (2H, s)],由以上數據推定TB-5為putra-

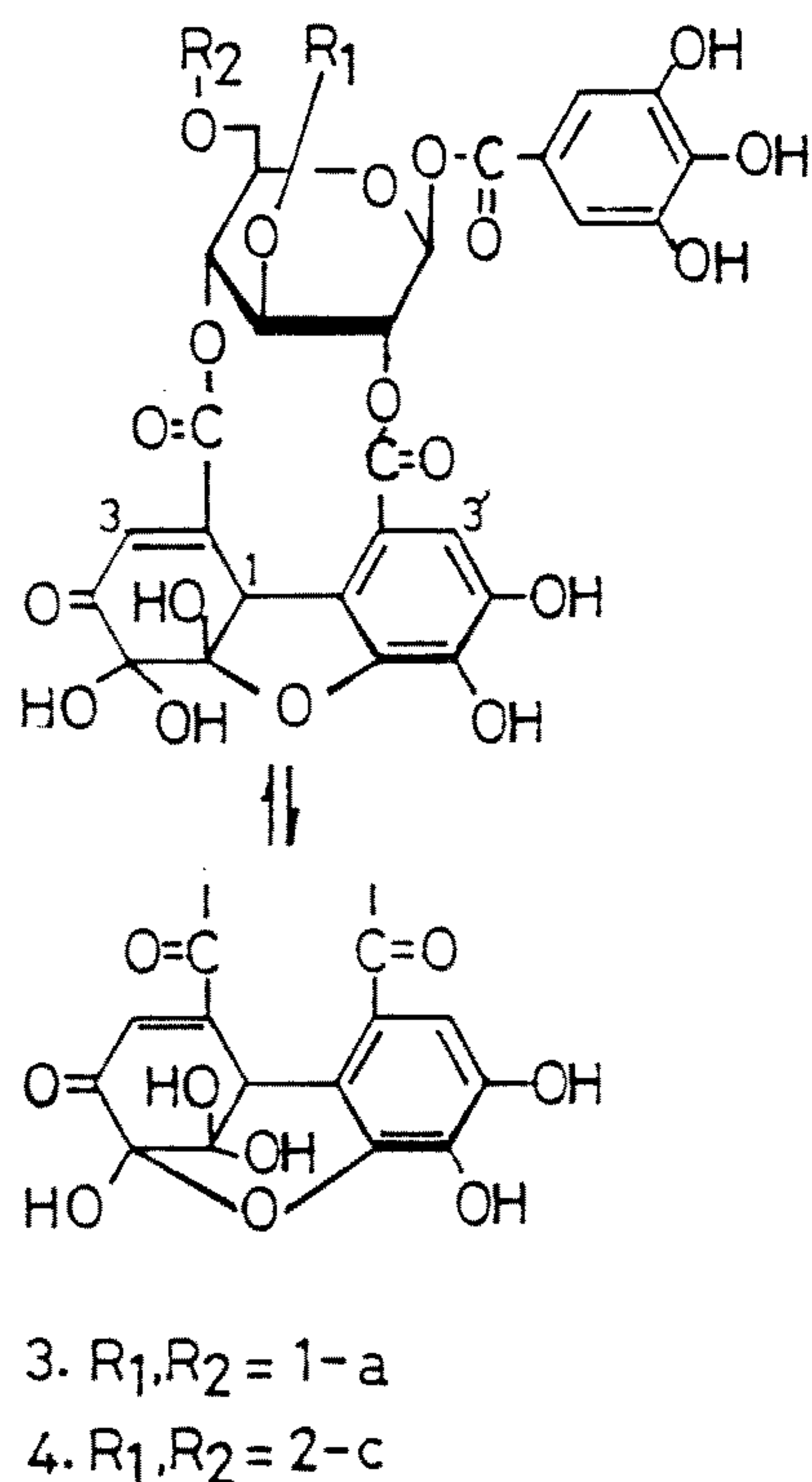


Figure 2. Structures of 3 and 4

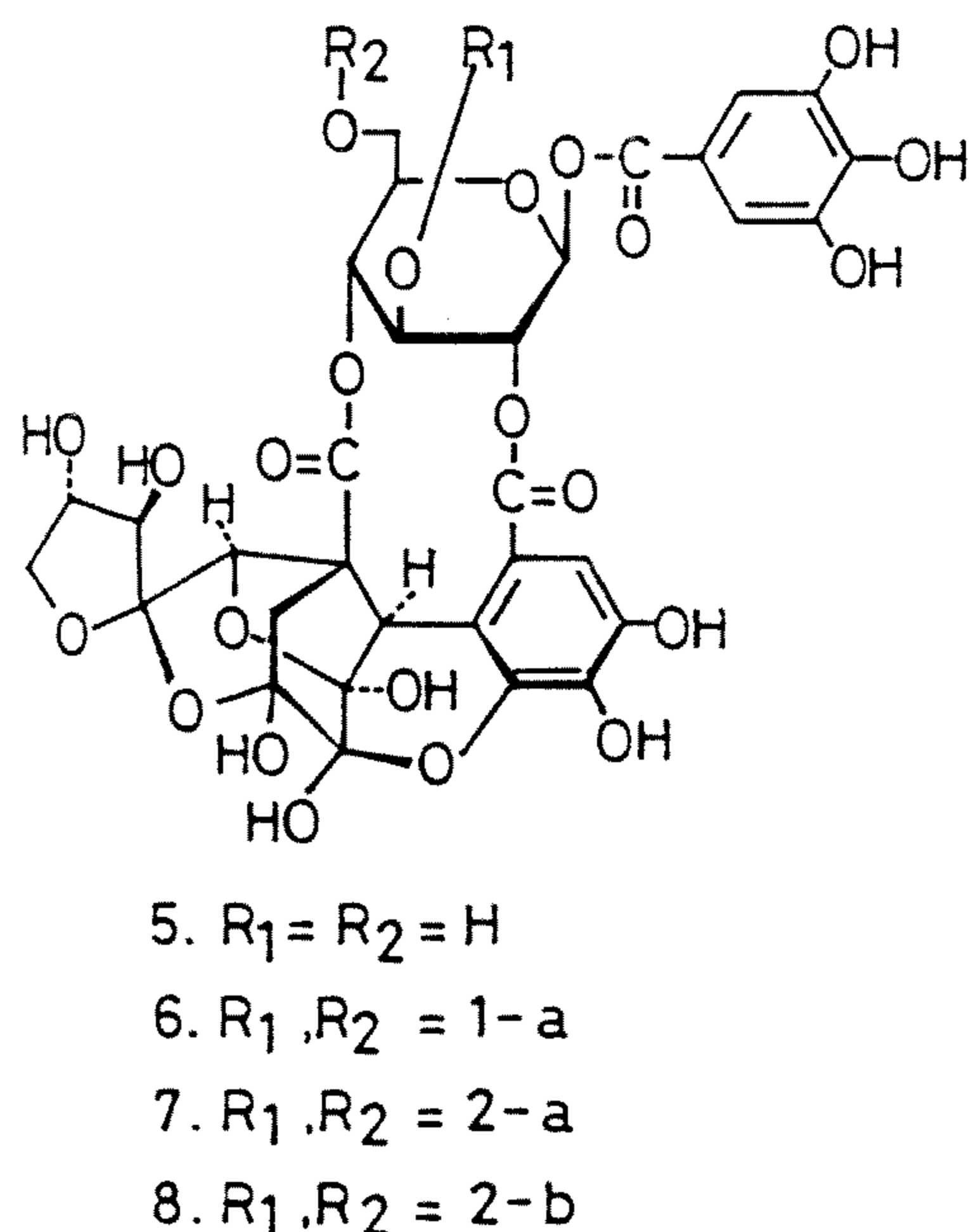


Figure 3. Structures of 5, 6, 7 and 8.

putranjivain B(5)⁽⁵⁾ 如圖三，經比對其¹H-NMR光譜及諸物理數據而確認之。

TB-6為無色板狀晶， $[\alpha]_D -62.0^\circ$ ；TB-7為淡褐色無晶形粉末， $[\alpha]_D -48.3^\circ$ ；TB-8為淡褐色無晶形粉末， $[\alpha]_D -7.3^\circ$ 。三者之¹H-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)歸屬為HHDP基之吸收峰。以上數據經與putranjivain A比較均一致而確認TB-6為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均為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mallo-tunin(7)⁽⁶⁾及mallophilinin(8)⁽⁷⁾比較¹H-NMR光譜及諸物理性質而確認TB-7為3, 6位接valoneayl基之mallotunin；TB-8為3, 6位接tergalloyl基之mallophilinin（如圖三）。

TB-9為淡褐色粉末， $[\alpha]_D -54.3^\circ$ ，其¹H-NMR光譜與neochebulagic acid比較，glucose之pattern極為類似[δ 6.23 (1H, d, $J=4$ Hz, H-1), 5.60 (1H, d, $J=4$ Hz, H-4), 4.88 (1H, $J=4$ Hz, H-3), 4.69 (1H, dd, $J=7, 10$ Hz, H-6), 4.60 (1H, t, $J=7$ Hz, H-

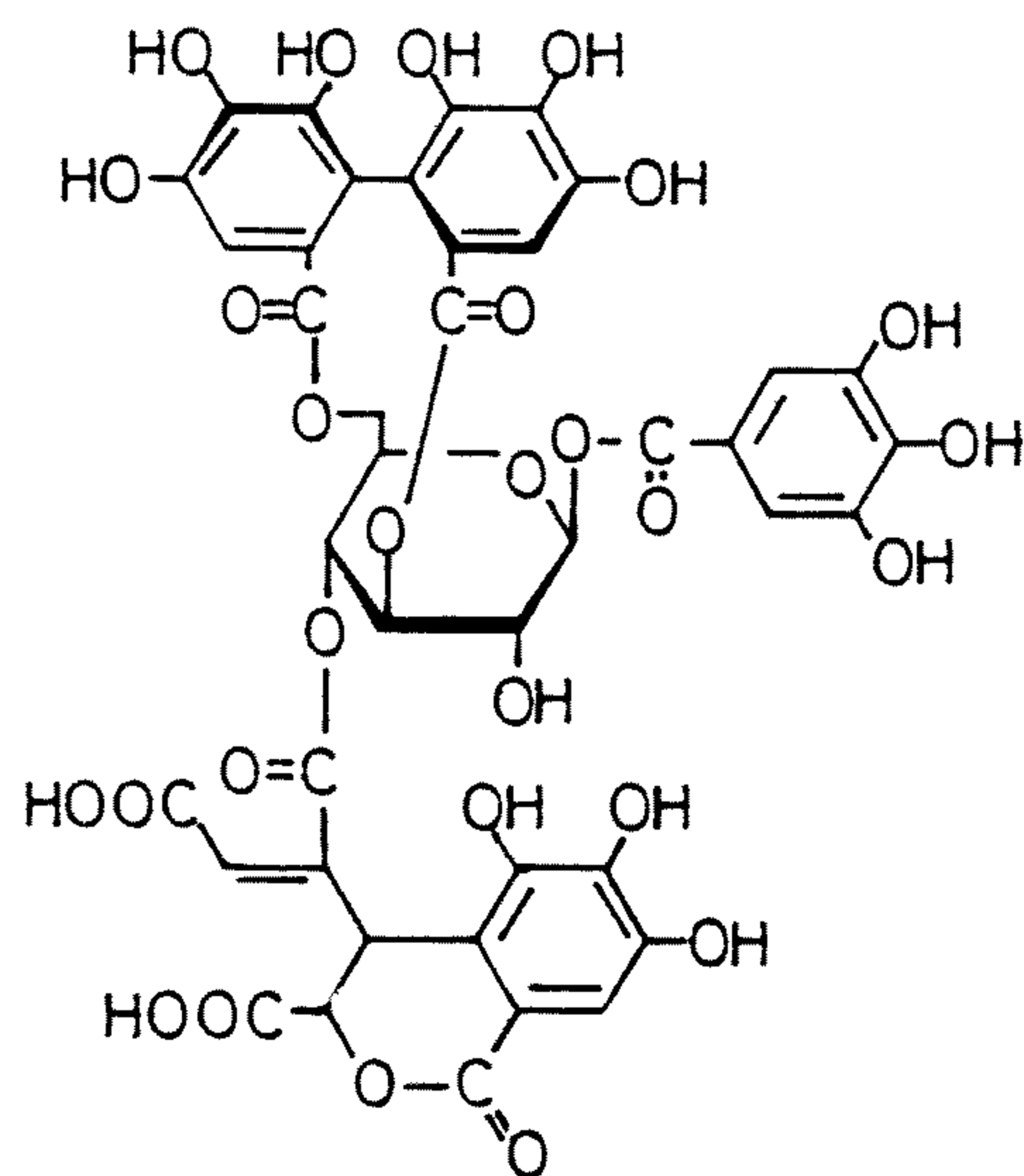


Figure 4. Structures of 9

5), 4.29 (1H, dd, $J=7, 10$ Hz, H-6), 4.27 (1H, d, $J=4$ Hz, H-2)]，顯示glucose之1, 3, 4, 6位之OH基均被醯基化，此外¹H-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)]，故可能為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, $J=2$ Hz, DCHE H-2, 3)呈現吸收峰，因此推測為glucose之4位為接4-dehydrochebuloyl基之repandusinic acid A,⁽⁸⁾經直接比對其諸物理數據及¹H-NMR光譜均完全一致而確認TB-9為repandusinic acid A(9)（如圖四）。

TB-10為淡褐色無晶形粉末， $[\alpha]_D -80.3^\circ$ ，¹H-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, $J=11$ Hz), 2.44 (1H, dd, $J=7, 11$ Hz)及 δ 4.61 (1H, dd, $J=7, 11$ Hz)呈現ABX型吸收峰，在 δ 4.83 (1H, s)呈現一個benzylmethine H之singlet；在 δ 7.10 (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¹³C-NMR光譜檢討，除了galloyl基，HHDP基及glucose之吸收訊號外，在 δ 46.3(t)呈現methylene；在 δ 63.2(d)及74.8(d)為methine；在 δ 78

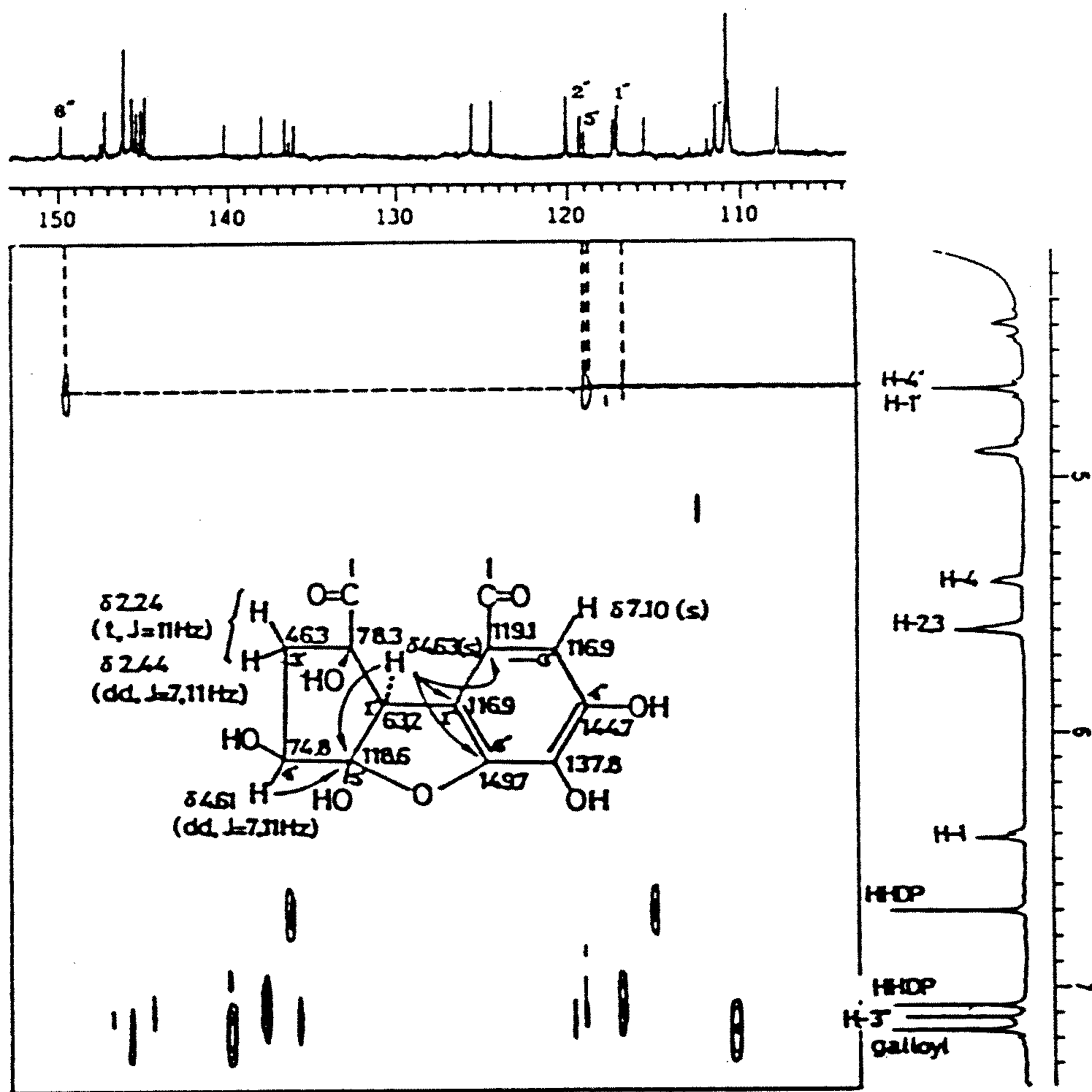


Figure 5. ^1H - ^{13}C Long-Range COSY Spectrum of 10 (in acetone- d_6 , Jch=8Hz)

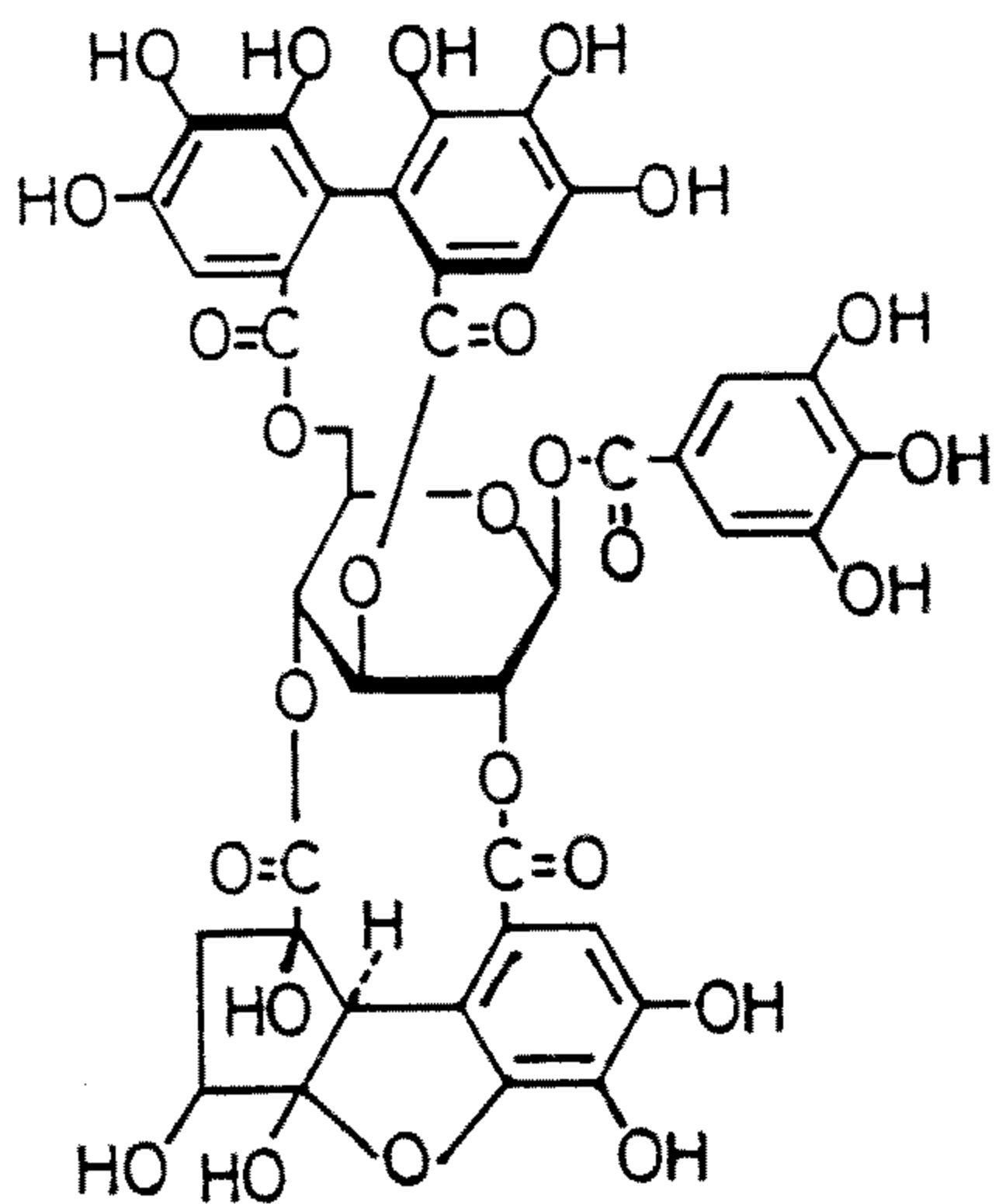


Figure 6. Structures of 10

3(s)則為四級碳之吸收訊號;此外,在 δ 116.9(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為類似。 δ 118.6之訊號依 ^1H - ^{13}C long-range COSY光譜(如圖五)所示,與 δ 4.61,及4.63之methine H具cross peak,可知為四級碳。綜合以上 ^1H -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,故而確認其為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¹C₄-(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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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), mallo-tunin(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.