
Studies on tannins from the bark of *Macaranga sinensis* (Baill.) Muell.-Arg.

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紅肉橙蘭樹皮部單寧成分之研究

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摘 要

紅肉橙蘭(*Macaranga sinensis*)之樹皮以含水丙酮冷浸萃取, 萃取液利用各種管柱層析, 分離得到 brevifolin carboxylic acid(1), corilagin(2), tercatain(3), mallorepanin(4), furosin(5), geraniin(6), macarinin A(7), chebulagic acid(8), macarinin B(9), putranjivain A(10), phyllanthusiin C(11), bixanin(12) 及 1-0-galloyl-2,4-(4-hydroxychebuloyl)-3,6-(R)-HHDP- β -D-glucopyranose(13)等13種化合物, 其中化合物13為新化合物。

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, 已知化合物並與文獻所載數據或標準品直接比對確認之。

前 言

在植物單寧(Tannin)成分研究系列中, 有關大戟科(Euphorbiaceae)植物血桐[*Macaranga taniarius* (L.) Muell.-Arg.] 及紅肉橙蘭 (*M. sinensis* (Baill.) Muell.-Arg.)之研究, 著者曾提出由血桐葉部分離得31種單寧成分,⁽¹⁾由其樹皮部分離得10種單寧成分⁽²⁾及由紅肉橙蘭葉部分離得18種單寧成分⁽³⁾之報告, 此次由紅肉橙蘭之樹皮部分離得13種化合物, 其中化合物13為新化合物, 本報告說明各化合物之構造決定。

材料與方法

一、材料

紅肉橙蘭樹皮(1987年10月台灣省林業試驗所呂勝由先生採集自蘭嶼並鑑定)

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), Bondapak C₁₈/Porasil B (37-75 μ , Waters Associates, Inc.)。

四、成分之萃取及分離

紅肉橙蘭樹皮部乾燥後(含小枝, 4.5 Kg), 用70%丙酮室溫下浸泡萃取, 萃取液於減壓下將丙酮除去, 析出之沈澱濾去後, 濾液減壓濃縮至約1 L, 利用Sephadex LH-20管柱層析(6.5 × 60 cm), 先以H₂O沖提, 再逐漸增加MeOH, 最後並加acetone沖提, 劃分成Fr. I(18 g), Fr. II(30 g)及Fr. III(43 g)三部分。Fr. I利用Sephadex LH-20管柱層析, 先以H₂O再逐漸增加MeOH沖提(以下以Sephadex LH-20/H₂O-MeOH表示), 再利用Sephadex LH-

20/EtOH純化,得到化合物1(32 mg).Fr.II利用Sephadex LH-20/H₂O-MeOH分成Fr.II-a及Fr.II-b兩部分,Fr.II-a利用Sephadex LH-20/80%MeOH分離得到化合物2 (180 mg), Fr II-b利用Sephadex LH-20/H₂O-MeOH, Sephadex LH-20/EtOH, MCI gel CHP 20P/H₂O-MeOH及Bondapak C₁₈/Porasil B/H₂O-MeOH, 分離得到化合物5(280 mg), Fr.III利用MCI gel CHP 20P/H₂O-MeOH分成a-e五個部分,各部分利用上述各種管柱層析,由Fr.III-a分離得到化合物10(350 mg),11(80 mg),由Fr.III-b分離得到化合物7(140 mg),由Fr.III-c分離得到化合物6(1.63 g),由Fr.III-d分離得到化合物3 (440 mg), 4(20 mg), 8(440 mg), 9(140 mg), 13 (120 mg),由Fr.III-e分離得到化合物12(70 mg),各化合物之性質及光譜數據如下:

化合物 1: Brevifolincarboxylic acid (1)

黃色粉末(H₂O-MeOH), mp > 300 °C, $[\alpha]_D^{25} -3.0^\circ$ (c=0.4, H₂O:acetone=2:3). ¹H-NMR (acetone-d₆+D₂O)δ 2.58 (1H, dd, J=18.9,1.8 Hz, H-5), 3.09 (1H, dd, J=7.8,18.9 Hz, H-5), 4.56 (1H, dd, J=7.8,1.8 Hz, H-4), 7.45 (1H, s, H-3').

化合物 2: Corilagin (2)

白色無晶形粉末, $[\alpha]_D^{21} -190.2^\circ$ (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), 4.85-5.08 (2H, m, H-3,6), 6.38 (1H, s, H-1), 6.69,6.84 (each 1H, s, HHDP H), 7.12 (2H, s, galloyl H).

化合物 3: Tercatain (3)

淡褐色無晶形粉末, $[\alpha]_D^{22} -73.0^\circ$ (c=0.9, acetone). ¹H-NMR (acetone-d₆)δ 4.35 (1H, d, J=4.2, Hz, H-2), 4.50-4.85 (3H, m, H-5,6), 5.04 (1H, d, J=3.4 Hz, H-3), 5.82 (1H, d, J=3.4 Hz, H-4), 6.36(1H, d, J=4.2 Hz, H-1), 6.84, 6.92 (each 1H, s, HHDP H), 7.02, 7.22 (each 2H, s, galloyl H).

化合物 4: Mallorepanin (4)

淡褐色無晶形粉末, $[\alpha]_D^{13} -63.0^\circ$ (c=0.5, MeOH). ¹H-NMR (acetone-d₆+D₂O)δ 4.40-4.65 (2H in total, m, H-4,5), 4.79-4.94 (2H in total, m, H-3,6), 6.39 (1H, d, J=2.4 Hz, H-1), 6.77, 6.79, 6.93 (each 1H, s, tergalloyl H), 7.15 (2H, s,

galloyl H).

化合物 5: Furosin (5)

黃色粉末(H₂O), mp 197-198 °C (dec.), $[\alpha]_D^{23} -142.1^\circ$ (c=1.0,MeOH). ¹H-NMR (acetone-d₆+D₂O)δ 5.34 (1H, s, DHHDP H-1), 6.46 (1H, d, J=0.8 Hz, H-1), 6.53 (1H, s, DHHDP H-3), 7.23 (2H, s, galloyl H), 7.28 (1H, s, DHHDP H-3').

化合物 6: Geraniin (6)

黃色粉末(H₂O), mp 218-221 °C (dec.), $[\alpha]_D^{22} -147.8^\circ$ (c=0.9,MeOH). ¹H-NMR (acetone-d₆+D₂O)δ 4.28-4.54 (1H, m, H-6), 4.68-5.00 (2H in total, H-5,6), 5.02 (1H, s, DHHDP H-1), 5.40-5.60 (3H in total, H-2,3,4), 6.53 (1H, s, DHHDP H-3), 6.59 (1H, s, H-1), 6.69, 7.12 (each 1H, s, HHDP H), 7.20 (2H, s, galloyl H), 7.23 (1H, s, DHHDP H-3').

化合物 7: Macarinin A (7)

淡黃色無晶形粉末, $[\alpha]_D^{15} -42.0^\circ$ (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 (1/3 H, d, J=1.5 Hz, 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=1.5 Hz, 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).

化合物 8: Chebulagic acid (8)

白色粉末(H₂O), mp 240 °C (dec.), $[\alpha]_D^{23} -54.3^\circ$ (c=1.0,acetone). ¹H-NMR (acetone-d₆)δ 2.21 [2H, d, J=7.6 Hz, chebuloyl (che) H-5], 3.88 (1H, dt, J=1.4,7.6,7.6 Hz, che H-4), 4.39 (1H, dd, J=14.2,12.3, Hz, H-6), 4.68-4.84 (2H in total, m, H-5,6), 4.92 (1H, d, J=7.1 Hz, che H-2), 5.12 (1H, dd, J=7.1,1.4 Hz, che H-3) 5.23 (1H, d, J=3.8 Hz, H-4), 5.52 (1H br. s, H-2), 5.96 (1H, br. s, H-3), 6.52 (1H, s, H-1), 6.65, 7.06 (each 1H, s, HHDP H), 7.13 (2H, s, galloyl H), 7.50 (1H, s, che H-3').

化合物 9: Macarinin B(9)

灰白色無晶形粉末, $[\alpha]_D^{25}$ -23.1° ($c=1.1$, MeOH). $^1\text{H-NMR}$ (acetone- d_6 + D_2O) δ 2.18 (2H, d, $J=8.0$ Hz, che H-5), 3.88 (1H, dt, $J=2.0, 8.0$ Hz, che H-4), 4.40-4.80 (2H m, H-6), 4.86 (1H m, H-5), 4.90 (1H, d, $J=7.6$ Hz, che H-2), 5.11 (1H, dd, $J=2.0, 7.1$ Hz, che H-3), 5.20 (1H, m H-4), 5.52 (1H, br. s, H-2), 5.95 (1H, br. s, H-3), 6.51 (1H, s, H-1), 6.73, 6.96, 7.00 (each 1H, s, aromatic H), 7.19 (2H, s, galloyl H), 7.52 (1H, s, che H-3').

化合物 10: Putranjivain A(10)

無色板狀晶(H_2O), mp 252-253 $^\circ\text{C}$ (dec.), $[\alpha]_D^{24}$ -62.0° ($c=1.0$, MeOH). $^1\text{H-NMR}$ (270MHz, acetone- d_6) δ 1.64 [1H, d, $J=14.7$ Hz, putranjivainoyl (put) H-3], 2.72 (1H, dd, $J=1.5, 14.7$ Hz, put H-3), 3.94 (1H, m, put H-5'), 4.17 (1H, br. s, put H-4'), 4.19 (1H, m, put H-5'), 4.25 (1H, s, put H-3'), 4.45 (1H, dd, $J=7.8, 11.4$ Hz, H-6), 4.72 (1H, dd, $J=8.5, 11.4$ Hz, H-6), 4.75 (1H, d, $J=1.5$ Hz, put H-1), 4.92 (1H, dd, $J=7.8, 8.5$ Hz, H-5), 5.05 (1H, s, put H-1'), 5.35 (1H, d, $J=3.9$ Hz, H-3), 5.61 (1H, s, H-2), 5.66 (1H, d, $J=3.9$ Hz, H-4), 6.53 (1H, s, H-1), 6.66, 7.08 (each 1H, s, HHDP H), 7.19 (2H, s, galloyl H), 7.32 (1H, s, put H-3').

化合物 11: Phyllanthusin C(11)

淡褐色無晶形粉末, $[\alpha]_D^{20}$ -80.3° ($c=0.8$, MeOH). $^1\text{H-NMR}$ (270MHz acetone- d_6) δ 2.24 (1H, t, $J=11.2$ Hz, 2,4-acyl H-3), 2.44 (1H, dd, $J=6.8, 11.2$ Hz, 2,4-acyl H-3), 4.37 (1H, dd, $J=12.8, 15.3$ Hz, H-6), 4.61 (1H, dd, $J=6.8, 11.2$ Hz, 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, $J=2.9$ Hz, H-4), 5.58 (2H, br. s, H-2,3), 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).

化合物 12: Bixanin(12)

淡褐色無晶形粉末, $[\alpha]_D^{18}$ -63.9° ($c=0.8$, MeOH). $^1\text{H-NMR}$ (270, MHz acetone- d_6) δ 4.80-4.89 (2H, m, H-5,6), 5.19 [1H, d, $J=6.6$ Hz, dehydrochebuloyl (DCHE) H-2], 5.35 (1H, br. s, H

-2), 5.38 (1H, br. s, H-4), 5.40 (1H, d, $J=4.2$ Hz, H-3), 5.52 (1H, d, $J=6.6$ Hz, DCHE H-3), 6.42 (1H, s, H-5), 6.70, 6.98 (each 1H, s, HHDP H), 6.85 (1H, s, H-1), 7.09 (1H, s, DCHE H-3'), 7.24 (2H, s, galloyl H).

化合物 13: 1-O-Galloyl-2,4-(4-hydroxychebuloyl)-3,6-(R)-HHDP- β -D-glucopyranose (13)

淡褐色無晶形粉末, $[\alpha]_D^{18}$ -32.9° ($c=0.7$, acetone). Anal. Calcd for $\text{C}_{41}\text{H}_{30}\text{O}_{28} \cdot 1/2\text{H}_2\text{O}$: C 50.26; H 3.19. Found : C 50.25; H, 3.24. negative FAB-MS m/z : 969 $[\text{M-H}]^-$. $^1\text{H-NMR}$ (270 MHz, acetone- d_6) δ 3.28 [1H, d, $J=16.4$ Hz, 4-hydroxychebuloyl (HCHE) H-5], 3.43 (1H, d, $J=16.4$ Hz, HCHE H-5), 4.43 (1H, dd, $J=8.2, 9.8$ Hz), 4.75 (1H, d, $J=9.8$ Hz), 4.81-4.89 (1H, m, H-5,6), 4.84 (1H, d, $J=5.7$ Hz, HCHE H-2), 4.90 (1H, d, $J=5.7$ Hz, HCHE H-3), 5.21 (1H, d, $J=4.1$ Hz, H-4), 5.55 (1H, d, $J=1.0$ Hz, H-2), 5.94 (1H, br. s, H-3), 6.56 (1H, br. s, H-1), 6.61, 7.05, 7.51 (each 1H, s, aromatic H), 7.18 (2H, s, galloyl H). $^{13}\text{C-NMR}$ (acetone- d_6 + D_2O) δ 42.5 (HCHE C-5), 47.3 (HCHE C-3), 62.2, 64.4, 67.4, 71.3, 74.1 (glc C-2~6), 68.5 (HCHE C-2), 77.6 (HCHE C-4), 91.9 (glc C-1), 107.7, 110.0 (HHDP C-3,3'), 110.6 (galloyl C-2,6), 115.0, 116.2, 117.2, 117.9 (HHDP C-1, 1', HCHE C-1',2', 3'), 119.8 (galloyl C-1), 124.2, 125.5 (HHDP C-2, 2'), 136.6, 138.8 (HHDP C-5,5'), 139.9, 140.1, 142.3 (galloyl C-4, HCHE C-4', 5'), 144.8, 145.0, 145.2, 145.4 (HHDP C-4, 4', 6,6'), 146.0 (galloyl C-3,5), 146.4 (HCHE C-6'), 165.4, 166.0, 166.5, 168.8, 169.7, 173.2, 174.1 (-COO-).

13-a: 褐色無晶形粉末, $[\alpha]_D^{18}$ -44.5° ($c=0.7$, acetone). Anal. Calcd for $\text{C}_{41}\text{H}_{28}\text{O}_{27} \cdot \text{H}_2\text{O}$: C 50.73; H 3.12. Found : C 50.58; H, 3.21. negative FAB-MS m/z : 951 $[\text{M-H}]^-$. $^1\text{H-NMR}$ (270 MHz, acetone- d_6 + D_2O) δ 2.91 (1H, d, $J=18.0$ Hz, HCHE H-5), 3.54 (1H, d, $J=18.0$ Hz, HCHE H-5), 4.40 (1H, dd, $J=14.8, 12.2$ Hz, H-6), 4.73-4.83 (2H in total, m, H-5,6), 5.19 (1H, d, $J=6.3$ Hz, HCHE H-3), 5.35 (1H, d, $J=2.6$ Hz, H-4), 5.59 (1H, br. s, H-2), 5.67 (1H, d, $J=6.3$ Hz, HCHE H-2), 5.73 (1H, m, H-3), 6.51 (1H, br. s, H-1), 6.65, 7.67 (each 1H, s, HHDP H), 7.16 (2H, s, galloyl

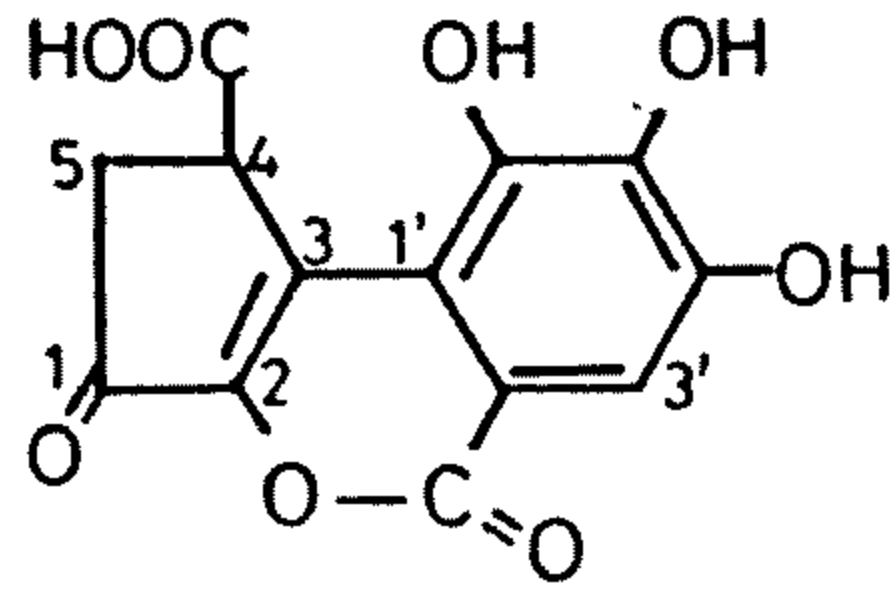


Figure 1. Structure of Compound 1

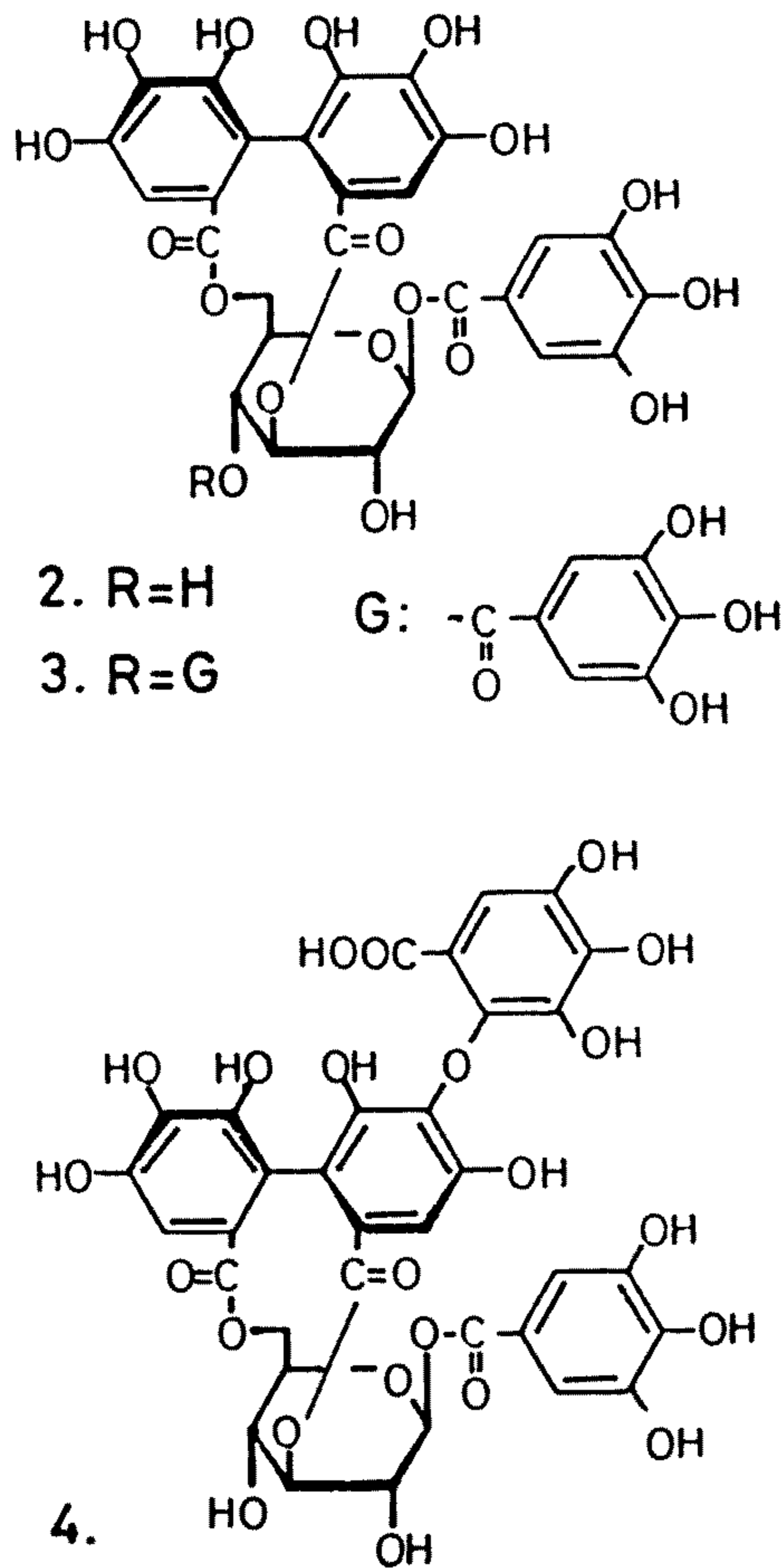


Figure 2. Structures of Compounds 2,3 and 4

H), 7.50 (1H, s, HCHE H-3').

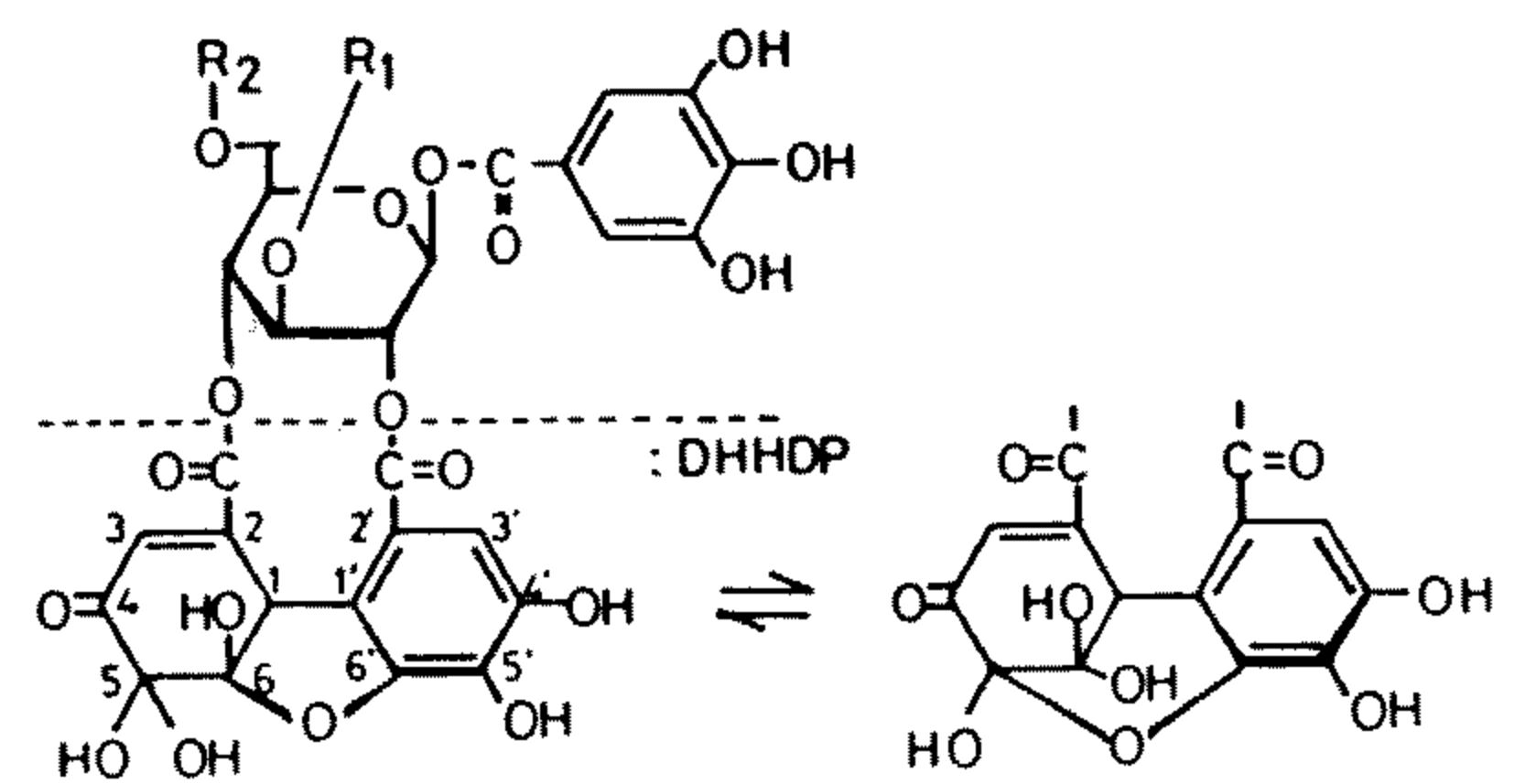
結果與討論

由紅肉橙蘭樹皮部分離到之13種單寧類化合物中, 化合物1為, phenylcarboxylic acid類化合物, 經與brevifolincarboxylic acid(1)標準品比較其比旋光度及氫核磁共振光譜(以下簡稱¹H-NMR

光譜)均一致, 而確認其構造如圖一。

化合物2,3,4為glucose之3,6位以醯基架橋之加水分解型單寧, 化合物2之¹H-NMR光譜, 在aromatic領域呈現一個hexahydroxydiphenoyl (HHDP)基[δ 6.69, 6.84 (each 1H, s)]及一個galloyl基[δ 7.12 (2H, s)]之訊號, anomeric H之訊號呈現在 δ 6.38 (1H, s), 光譜其他訊號及其諸性質亦均與corilagin (2)⁽¹⁾所呈現者一致, 化合物3之¹H-NMR光譜, 在aromatic領域呈現一個HHDP基[δ 6.84, 6.92 (each 1H, s)]及二個galloyl基[δ 7.02, 7.22 (each 2H, s)]之訊號, 與corilagin比較glucose之吸引訊號, anomeric H呈現在 δ 6.36 (1H, d, J=4.2 Hz), 另外在 δ 5.82 (1H, d, J=3.4 Hz)呈現可歸屬為glucose之H-4之訊號, 亦即corilagin之母核glucose之4位結合galloyl基之tercatin(3), 化合物2,3分別與corilagin, tercatin標準品直接比較確認之。化合物4之¹H-NMR光譜, 在aliphatic領域與corilagin非常類似, 顯示為1,3,6位取代之glucose為母核, 而3,6位呈結合醯基之架橋, 在aromatic領域中, 呈現三個1H之單峰訊號[δ 6.77, 6.79, 6.93]及一個2H之單峰訊號[δ 7.15], 故推測為glucose之1位接galloyl基, 3,6位為接triphenoylcarboxylic acid之1-O-galloyl-3,6-(R)-tergalloyl- β -D-glucopyranose (mallorepanin), 與標準品比較光譜及性質均相同而確定構造為4⁽³⁾。

化合物5,6均為黃色結晶, 其¹H-NMR光譜均



5. R₁=R₂=H
6. R₁, R₂=HHDP
7. R₁, R₂=TER

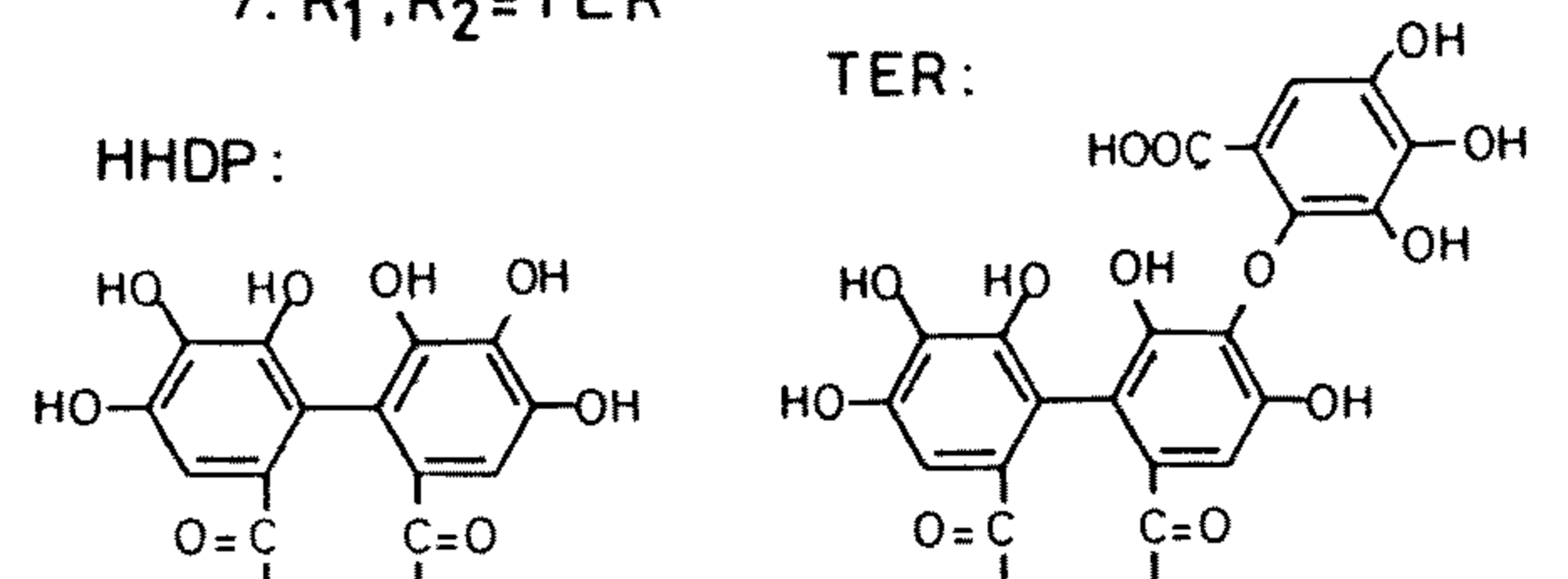


Figure 3. Structures of Compounds 5,6 and 7

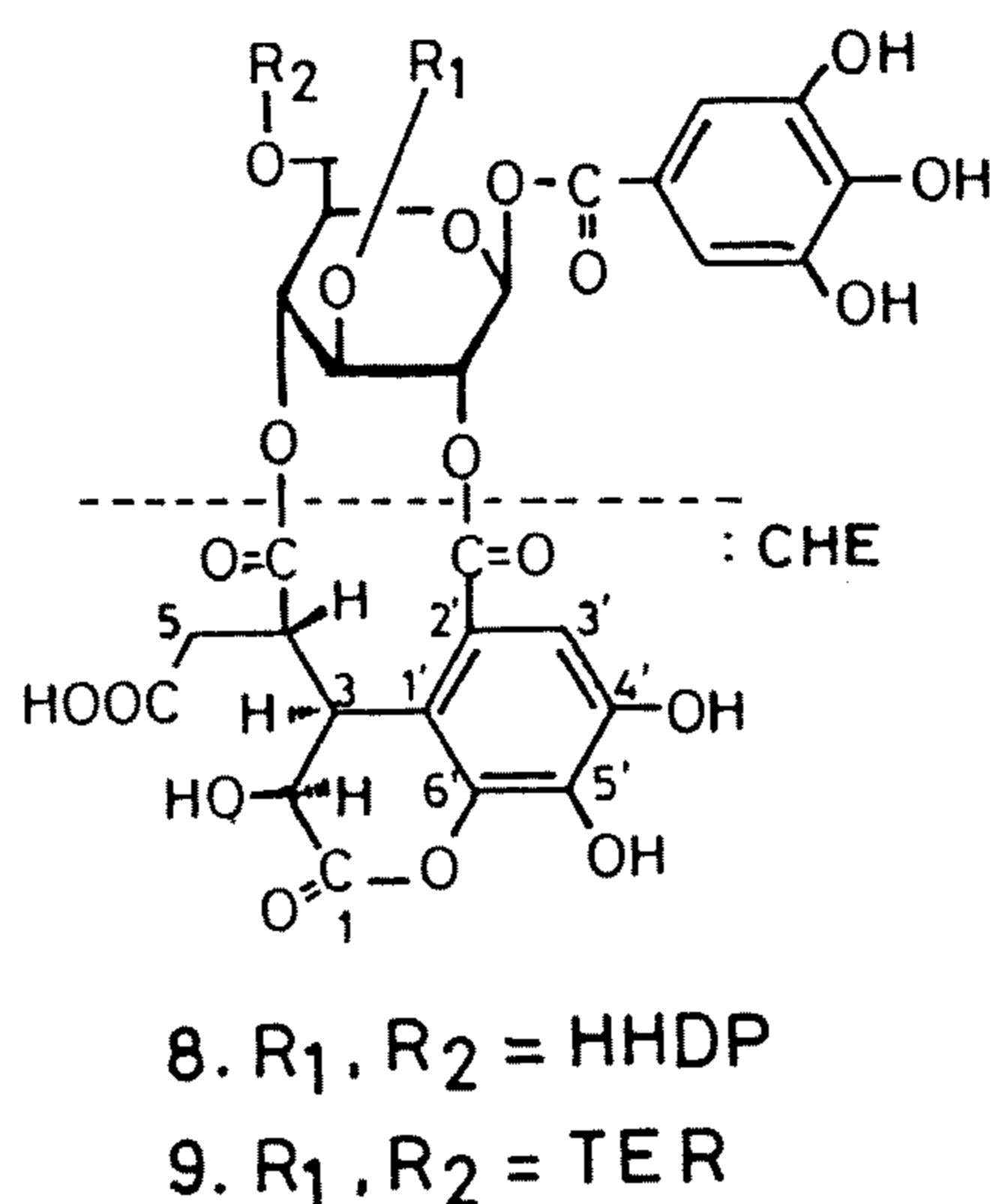
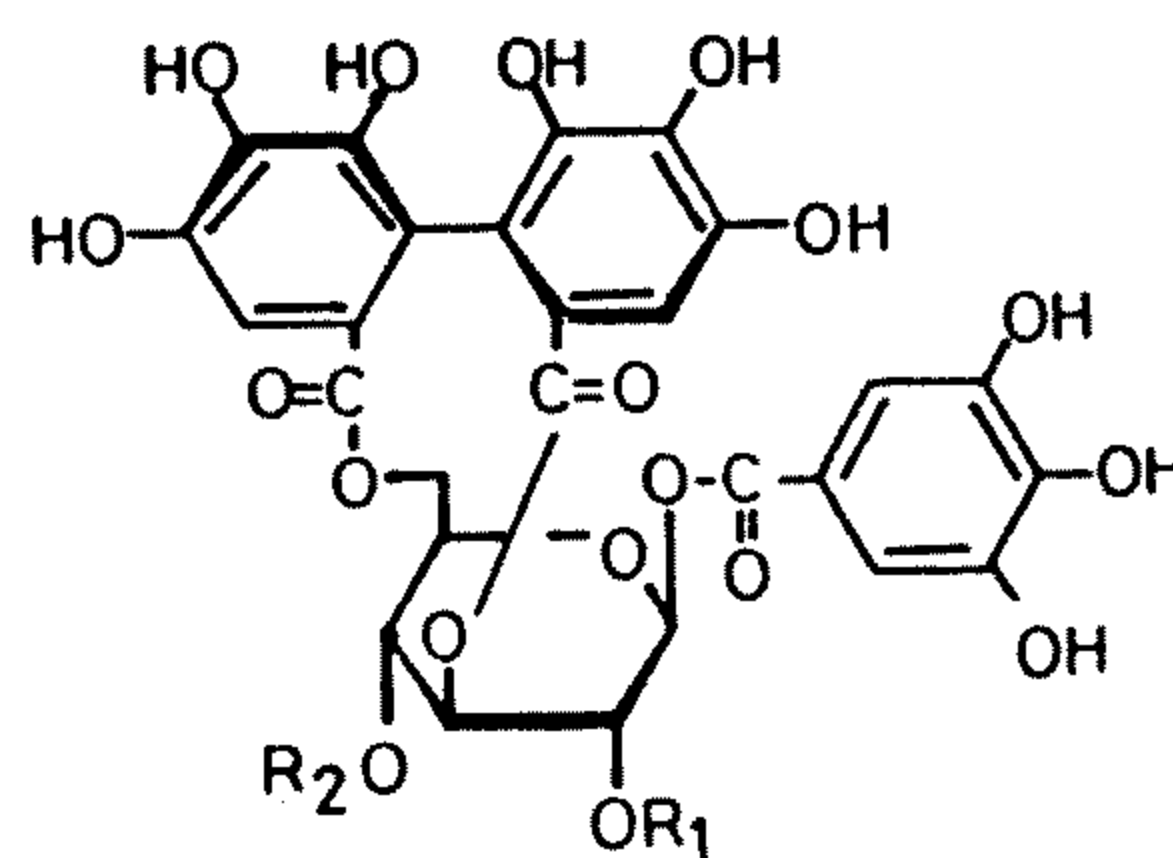


Figure 4. Structures of Compounds 8 and 9

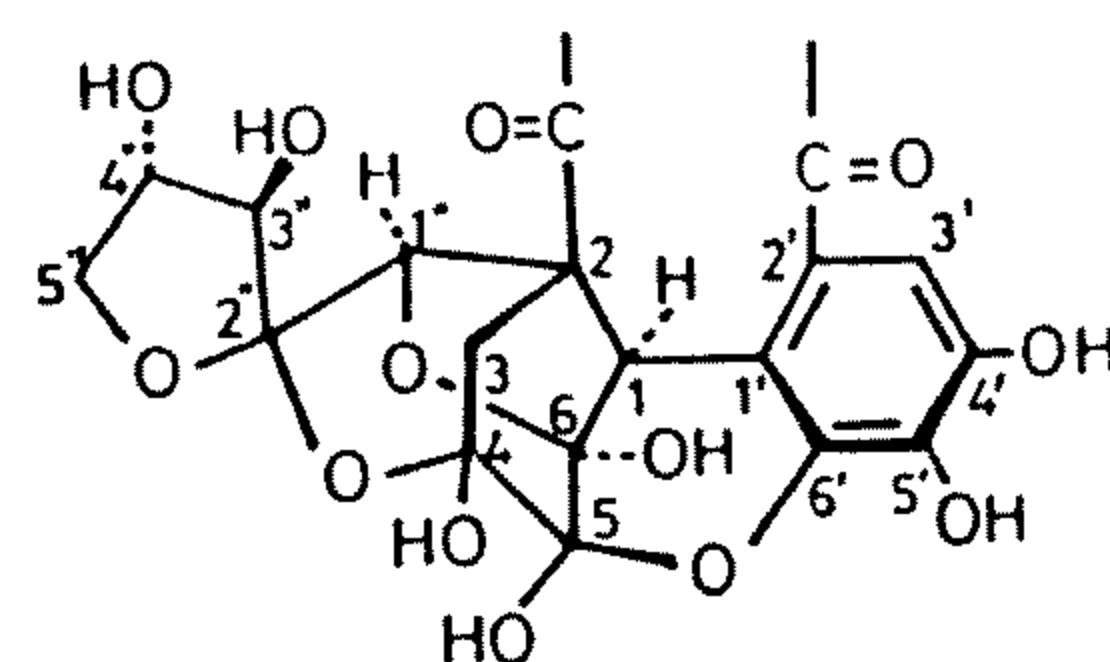
呈現dehydrohexahydroxydiphenoyl (DHHDP)基6員環狀態之特有吸收訊號[(5 : δ 5.34 (1H, s, DHHDP H-1), 6.53 (1H, s, DHHDP H-3), 7.28 (1H, s, DHHDP H-3'); 6 : δ 5.02 (1H, s, DHHDP H-1), 6.53 (1H, s, DHHDP H-3), 7.23 (1H, s, DHHDP H-3')],此外,化合物5在aromatic領域呈現一個galloyl基之吸收訊號,anomeric H之吸收訊號則呈現在 δ 6.46 (1H, d, $J=0.8$ Hz),諸性質及光譜數據直接與furosin(5)標準品比對均一致而確認其構造⁽¹⁾,化合物6則在aromatic領域中除galloyl基[δ 7.20 (2H, s)],之吸收訊號外,尚呈現HHDP基[δ 6.69, 7.12 (each 1H, s)]之吸收,與geraniin(6)標準品比較,而確認其構造如6⁽¹⁾。

化合物7為黃色無晶形粉末,其¹H-NMR光譜呈現DHHDP基之5員環及6員環平衡狀態特有之吸收峰[δ 4.94 (1/3H, d, $J=1.5$ Hz, DHHDP H-1), 5.17 (2/3H, s, DHHDP H-1), 6.25 (1/3H, d, $J=1.5$ Hz, DHHDP H-3), 6.53 (2/3H, s, DHHDP H-3)],經與macarinin A(7)直接比較完全一致而確認之⁽³⁾。

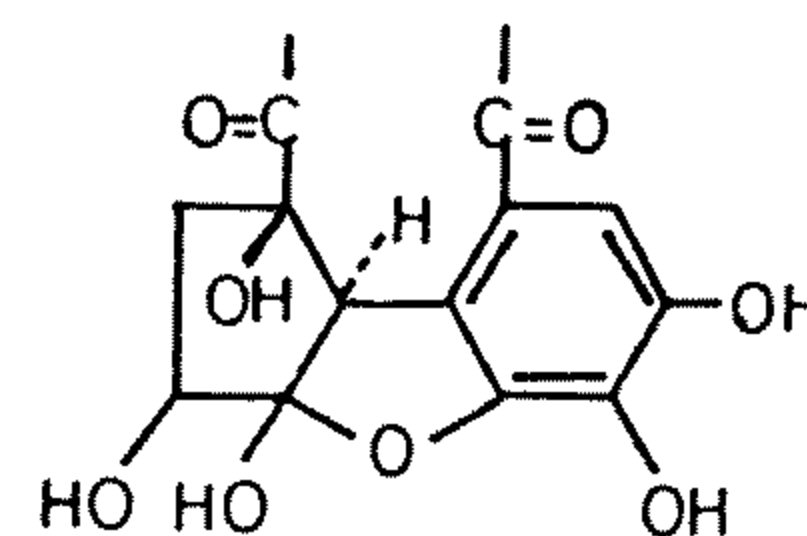
化合物8為白色結晶性粉末,化合物9為灰白色粉末,兩者之¹H-NMR光譜均呈現chebuloyl(che)基之吸收訊號[8 : δ 2.21 (2H, d, $J=7.6$ Hz, che H-5)] 3.88 (1H, dt, $J=7.6, 1.4$ Hz, che H-4), 4.92 (1H, d, $J=7.1$ Hz, che H-2), 5.12 (1H, dd, $J=7.1, 1.4$ Hz, che H-3), 7.50 (1H, s, che H-3'); 9 : δ 2.18 (2H, d, $J=8.0$ Hz, che H-5), 3.88 (1H, dt, $J=8.0, 2.0$ Hz, che H-4), 4.90 (1H, d, $J=7.6$ Hz,



10. $R_1, R_2 =$



11. $R_1, R_2 =$



12. $R_1, R_2 =$

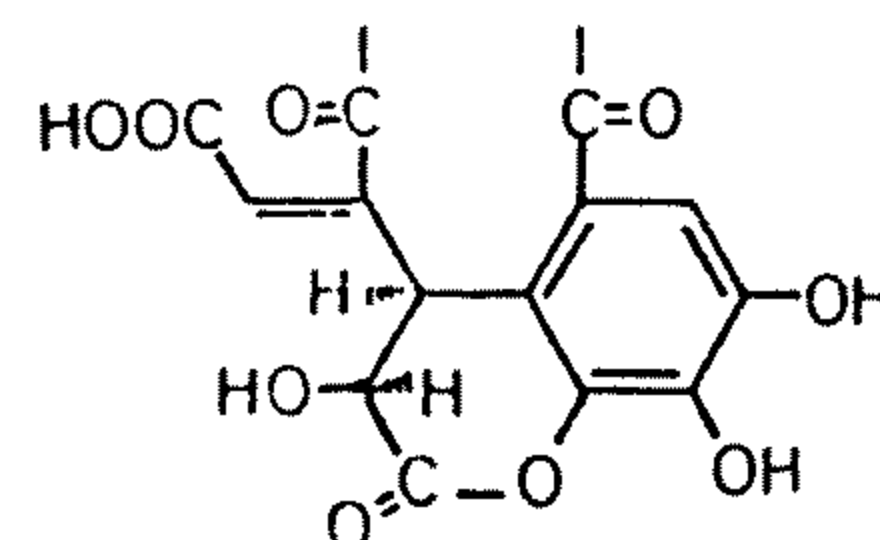


Figure 5. Structures of Compounds 10,11 and 12

che H-2), 5.11 (1H, dd, $J=2.0, 7.0$ Hz che H-3), 7.52 (1H, s, che H-3')],糖之anomeric H均呈現在 δ 6.52 (1H, s),且糖之氫核之吸收訊號均呈現在較低磁場,顯示均為醯基化。

化合物8在aromatic領域呈現二個1H [δ 6.65, 7.06 (each 1H, s)]及一個2H [δ 7.13 (2H, s)]之吸收訊號。因此,與糖結合之醯基,除了chebuloyl基外還有一個HHDP基及一個galloyl基,而化合物9在aromatic領域則呈現三個1H [δ 6.73, 6.96, 7.00 (each 1H, s)]及一個2H [δ 7.19 (2H, s)]之吸收訊號,故推測具有一個triphenoylcarboxyl基及一個galloyl基。化合物8,9分別與chebulagic acid (8)及macarinin B(9)比較完全一致故確認其構造。⁽³⁾

化合物10為無色板狀結晶, mp. 252-256 °C (dec),化合物11,12均為淡褐色無晶狀粉末,三者均呈現HHDP基之吸收[10 : δ 6.66, 7.08; 11 : δ

6.68, 7.05; **12** : δ 6.70, 6.98; (each 1H, s)], 糖之 anomeric H 各呈現於 δ 6.53; δ 6.40 及 δ 6.85 (each 1H, s), 其餘之氫訊號均呈現於較低磁場, 顯示各羥基均被醯化, 化合物 **10** 之 $^1\text{H-NMR}$ 光譜除上述吸收訊號外, 更呈現 putranjivainoyl (put) 基之吸收訊號 [δ 4.75 (1H, d, $J=1.5$ Hz, put H-1), 1.64 (1H,

d, $J=14.7$ Hz, put H-3), 2.72 (1H, dd, $J=1.5, 14$ Hz, put H-3), 5.05 (1H, s, put H-1''), 4.25 (1H, s, put H-3''), 4.17 (1H, br. s, put H-4''), 3.94, 4.19 (each 1H, m, put H-5'') 及 7.32 (1H, s, put H-3)], 故推定為 putranjivain A (**10**)⁽⁵⁾; 化合物 **11, 12** 亦由其 $^1\text{H-NMR}$ 光譜及物理化學性質各推定為 phylla-

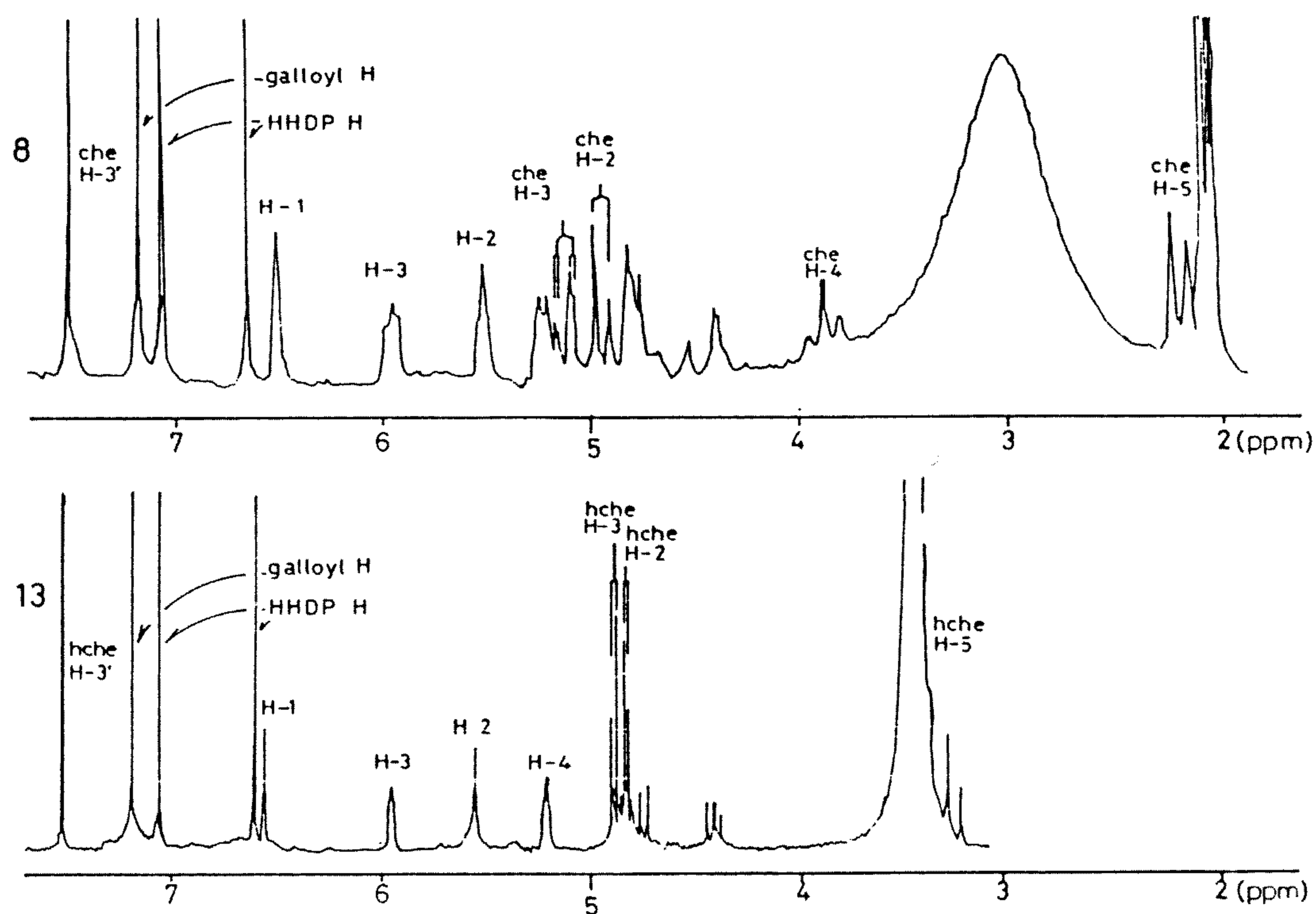


Figure 6. $^1\text{H-NMR}$ Spectra of Compounds 8 (100 MHz) and 13 (270 MHz) (in acetone- d_6)

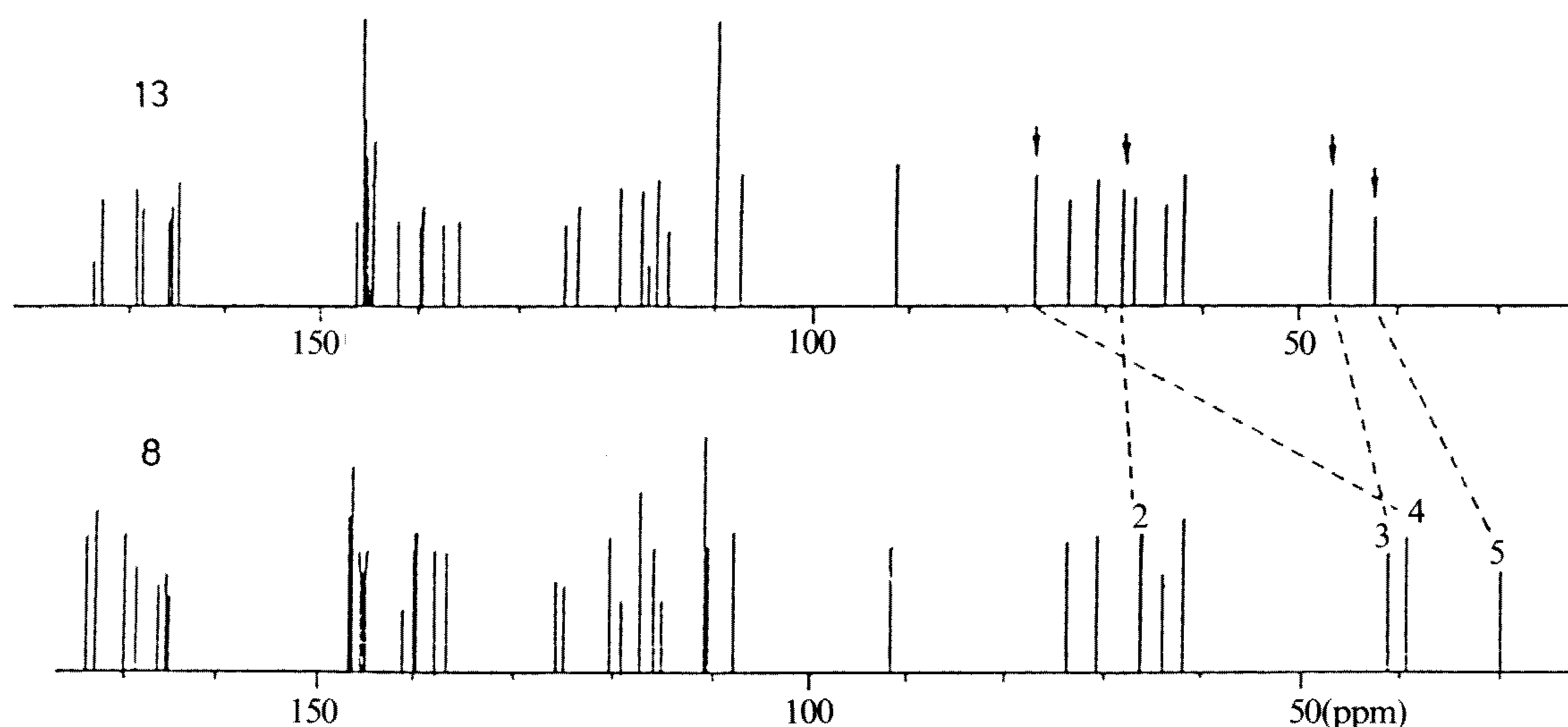


Figure 7. $^{13}\text{C-NMR}$ Spectra of Compounds 13 and 8 (in acetone- d_6)

nthusiin C(11)⁽⁶⁾及bixanin(12)⁽⁷⁾,以上推定之構造並經與標準品直接比較而確認之。

化合物13為淡褐色無晶形粉末, $[\alpha]_D^{25} -32.9^\circ$ (acetone), 元素分析確認其分子式為 $C_{41}H_{30}O_{28} \cdot 1/2 H_2O$, 其¹H-NMR光譜(圖6)呈現galloyl基[δ 7.18 (2H, s)], HHDP基[δ 6.61, 7.05 (each 1H, s)]及糖[anomeric H: δ 6.56 (1H, s)]之吸收訊號, 這些訊號之化學位移與由chebulagic acid(8)而來之數據非常相近, 顯示糖之羥基均被醯化, 且糖之1, 3, 6位之結合與chelulagic acid同為1位有galloyl基, 3, 6位為(R)HHDP之結合, 此外, ¹H-NMR光譜在 δ 3.28, 3.43 (each 1H, d, $J=16.4$ Hz)呈現一對互相偶合之亞甲基氫(methylene H); 在 δ 7.51 (1H, s)]呈現一個aromatic H之訊號。

化合物13之negative FAB MS圖譜在 m/z 969顯示其 $[M-H]^-$ 之peak, 此比chebulagic acid(8)之分子量多16 unit, 相當於一個氧原子, 此外, 比較¹³C-NMR光譜(圖7), 顯示兩者在aromatic領域之訊號及由糖而來之訊號甚為類似, 但chebuloyl基於 δ 39.5由methine而來之訊號, 在化合物13則呈現在 δ 77.6, 並為帶有羥基之4級碳, 此外在 δ 68.5, 47.3之二個由methine及 δ 42.5由methylene而來之訊號, 分別歸屬為相當於chebuloyl基之2, 3, 5位之碳素而來之訊號, 由以上之數據推測化合物13為4-hydroxychebulagic acid。

化合物13於室溫下放置, 則易脫水閉環生成13-a [negative FAB MS: m/z 951 $[M-H]^-$], 此由13-a與13之¹H-NMR光譜(圖6)比較之, 發現其糖及aromatic H之訊號極為類似, 但由chebuloyl基之H-2而來之訊號則往低磁場移動(13: δ 4.84; 13-a: δ 5.67), 再者, 5位之亞甲基氫之訊號分別於 δ 2.91, 3.54 (each 1H, d, $J_{gem}=18.0$ Hz), 由此而推定lactone係由chebuloyl基2位之羥基與6位羧基間脫水閉環形成 δ -lactone。

有關4-hydroxychebuloyl基之絕對配置係由化合物13之NOESY圖譜(圖8)中, chebuloyl基之benzyl methine (H-3)與glucose之anomeric H之間呈現強NOE, 而以Drieding model檢討之結果, 推測如13。

紅肉橙蘭之樹皮部所含之單寧以geraniin (3)為主成分, 且均為以¹C₄(或shew form)-conformation之glucose為母核之加水分解型單寧, 其2, 4位及3, 6位結合為多樣之醯基如: HHDP基, DHHDP基, chebuloyl基, tergalloyl基, putranjivainoyl基等。

在血桐而言, 由樹皮部得到之putranjivain A,

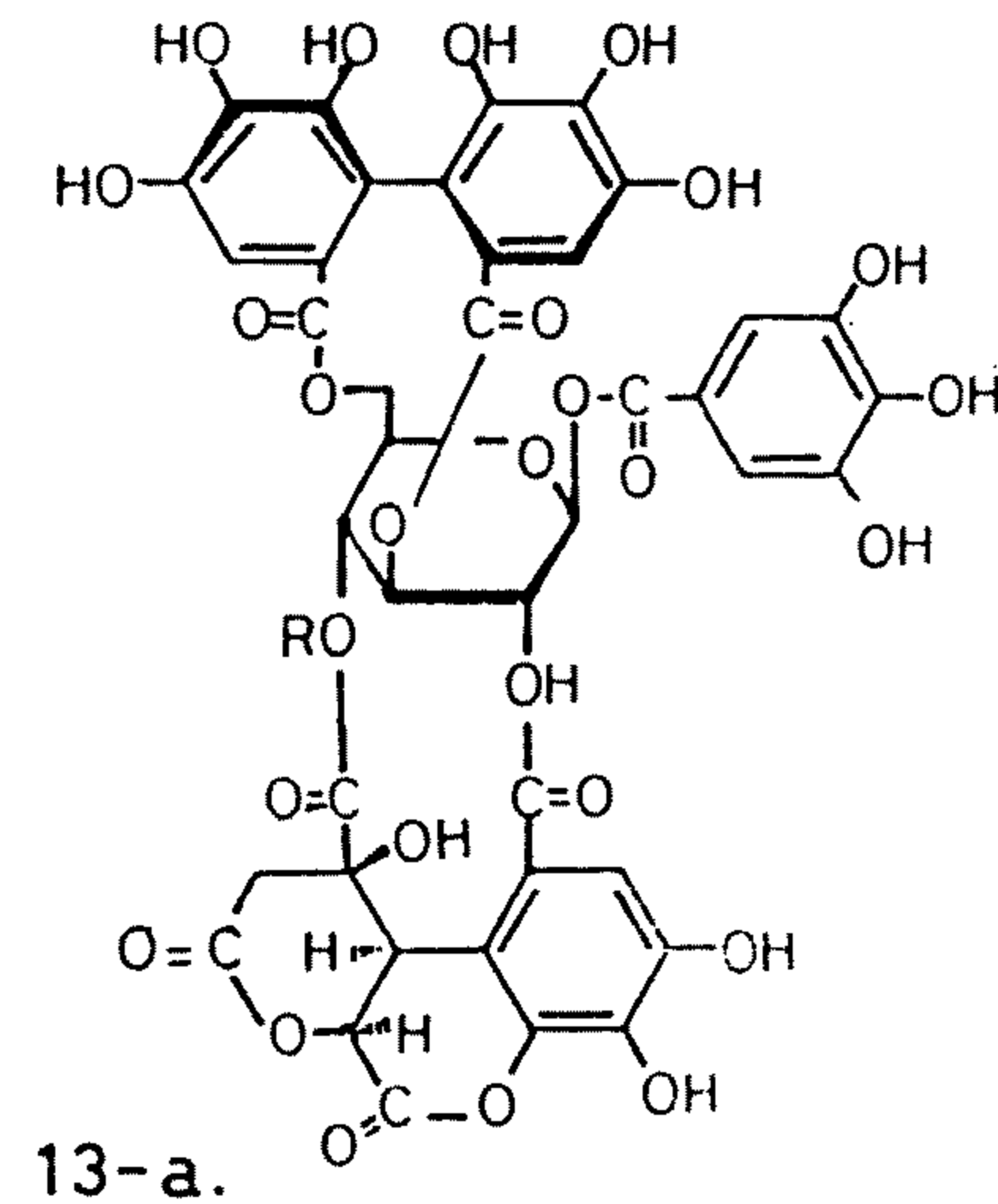
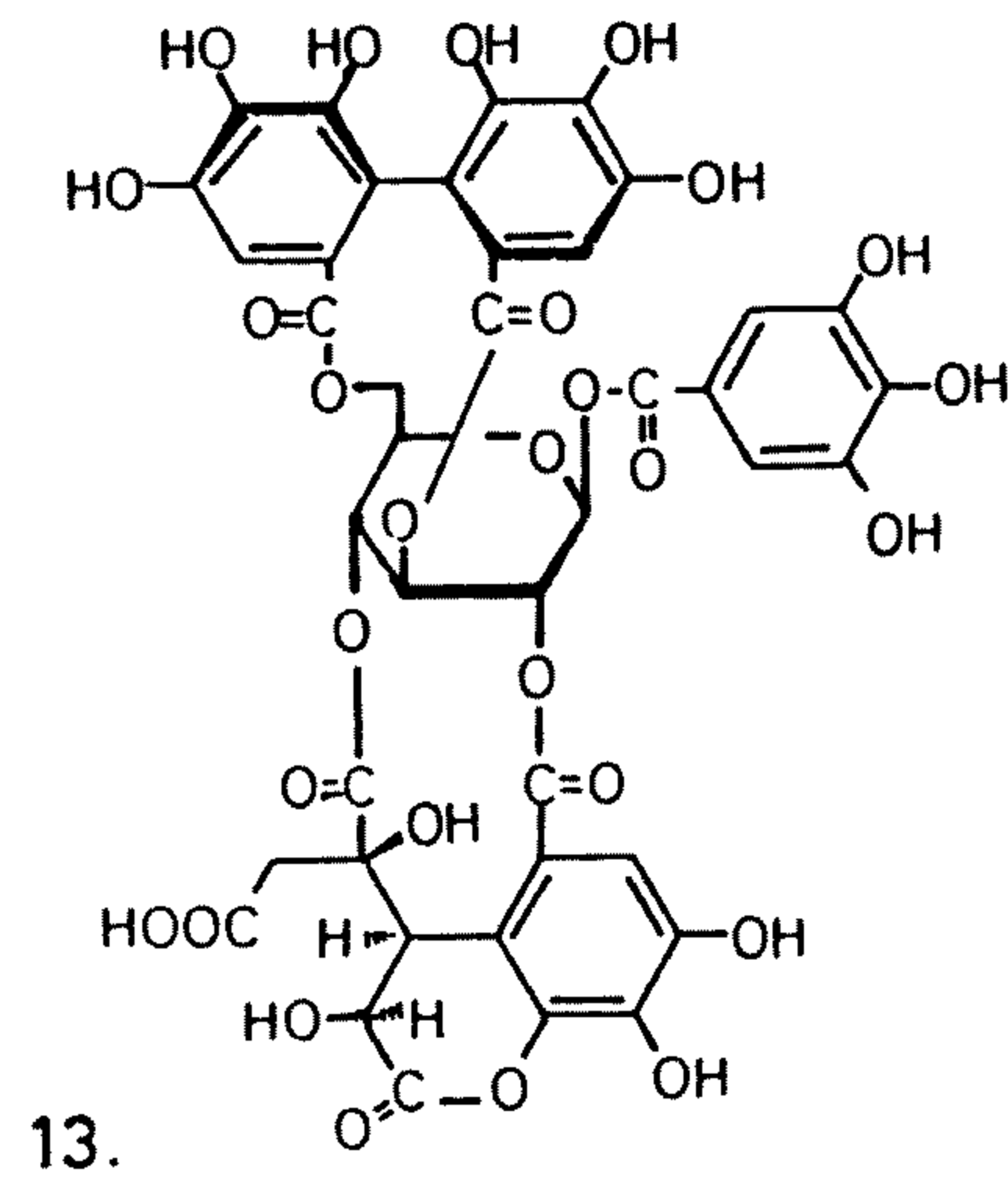


Figure 8. Structures of Compounds 13 and 13-a

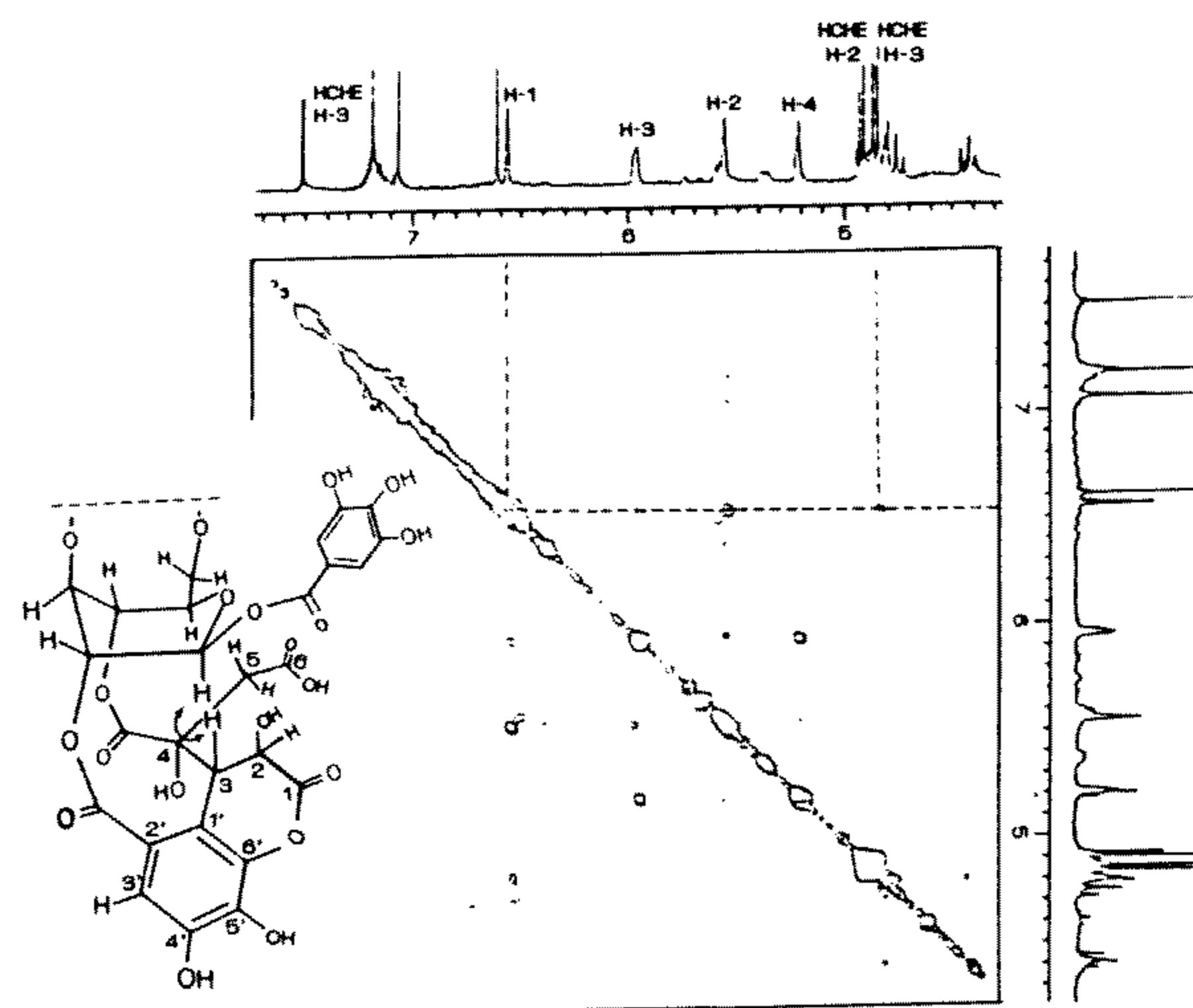


Figure 9. NOESY Spectrum of Compound 13

B, macarinin A及mallophilin,在葉部均未得到,而葉部所含之多種gallotannin在樹皮部則未得到,顯示不同部位之單寧呈現不同之氧化階段,而紅肉橙蘭與血桐亦有相同之情形,即在葉部與樹皮部所含之單寧成分不盡相同,如在葉部單離得含macaranoyl基之單寧,在樹皮部並未得到,而在樹皮部得到之bixanin, phyllanthusiin C及1-O-galloyl-2,4-(4-hydroxychebuloyl)-3,6-(R)-HHDP- β -D-glucopyranose(13)則未在葉部得到,顯然可見, *Macaranga*屬之二種植物及植物之不同部位,所含成分之差異甚大。

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Studies on Tannins from the Bark of *Macaranga sinensis* (Baill.) Muell.-Arg.

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ABSTRACT

Together with twelve known compounds—brevifolincarboxylic acid(1), corilagin(2), tercatain(3), mallorepanin(4), furosin(5), geraniin(6), macarinin A(7), chebulagic acid(8), macarinin B (9), putranjivain A(10), phyllanthusiin C(11), bixanin(12), a new hydrolyzable tannin, 1-0-galloyl-2,4-(4-hydroxychebuloyl)-3,6-(R)-HHDP-

β -D-glucopyranose(13) was isolated from the bark of *Macaranga sinensis* (Baill.) Muell.-Arg. (Euphorbiaceae).

Structures of these tannins were established on the basis of their physical properties and spectroscopic evidence.

Key Words: *Macaranga sinensis*, Euphorbiaceae, Hydrolyzable tannin.

