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THREE CAFFEYOYL TANNINS FROM *ILEX ROTUNDA*

by

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Abstract

Three known caffeoyl tannins, 1-caffeoylquinic acid, neochlorogenic acid and chlorogenic acid, have been isolated as acetates from the butanol extract of the fruits of *Ilex rotunda*.

Introduction

There are some reports on the constituents of *Ilex rotunda* (Aquifoliaceae), rotundic acid from the seeds¹⁾ and peduncloside from the leaves.²⁾ We have also isolated some new triterpenoids, rotungenic acid, rotundioic acid and rotungenoside, from the fruits.^{3),4)} A further study on the polar constituents of this fruits has now resulted in the identification of three known caffeoyl tannins, which were isolated as acetates. This paper describes the isolation and structure elucidation of them.

Results and Discussion

The methanol extract of the unripe fruits of *Ilex rotunda* was fractionated with ethyl acetate and butanol. Extensive chromatography of the butanol extract afforded a non triterpenoid fraction which was acetylated to give three acetates **1a**, **2a** and **3a**.

Compound **1a**, mp 177°C, needles from acetone-hexane, showed a molecular ion at m/z 504 $[M]^+$ corresponding to $C_{24}H_{24}O_{12}$ in the mass spectrum. Its IR spectrum exhibited the presence of 5-membered lactone (1810 cm^{-1}), ester (1750 cm^{-1}), double bond (1640 cm^{-1}) and phenyl groups (1500 cm^{-1}). The UV spectrum showed a conjugated system at 220 (ϵ 9000) and 283 nm (ϵ 13000) attributable to a sinnamoyl group. From the ^1H NMR (400 MHz, CDCl_3) data (Table 1), two alcoholic (δ 1.98 and 2.16) and two phenolic acetyl groups (δ 2.33) were observed along with a characteristic diacetylcaffeoyl group, identified by two trans olefinic protons at δ 6.34 (d, $J=16.5\text{Hz}$) and 7.68 (d, $J=16.5\text{Hz}$) and three aromatic protons of

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Table 1. ¹H NMR Data of Compounds **1a**, **2a** and **3a**

H	1a (400MHz)			2a (100MHz)			3a (400MHz)		
	δ	Mult	J/Hz	δ	Mult	J/Hz	δ	Mult	J/Hz
2a	2.63	d	11.3	2.60	d	12	2.40	dd	16, 3.6
2b	3.13	ddd	11.3, 6.6, 2.5	3.16	dd	12, 6	2.7	m	
3	4.93	dd	6.6, 4.5	4.96	dd	6, 4	5.56	td	9.6, 5.0
4	5.60	t	4.5	5.62	t	4	5.12	dd	9.6, 3.6
5	5.23	ddd	11.1, 7.8, 4.5	5.34	ddd	12, 8, 4	5.59	quint	3.6
6	2.3	m		2.35	m		2.7	m	
2'	7.43	br s		7.43	s		7.36	d	1.5
5'	7.27	d	9.0	7.32	d	8	7.22	d	8.0
6'	7.44	br d	9	7.50	d	8	7.39	dd	8.0, 1.5
7'	7.68	d	16.5	7.76	d	16	7.60	d	16.0
8'	6.43	d	16.5	6.40	d	16	6.32	d	16.0
Ac	1.98	s		2.16	s		2.00	s	
	2.16	s		2.16	s		2.08	s	
	2.33	s		2.32	s		2.14	s	
	2.33	s		2.32	s		2.29	s	
							2.30	s	

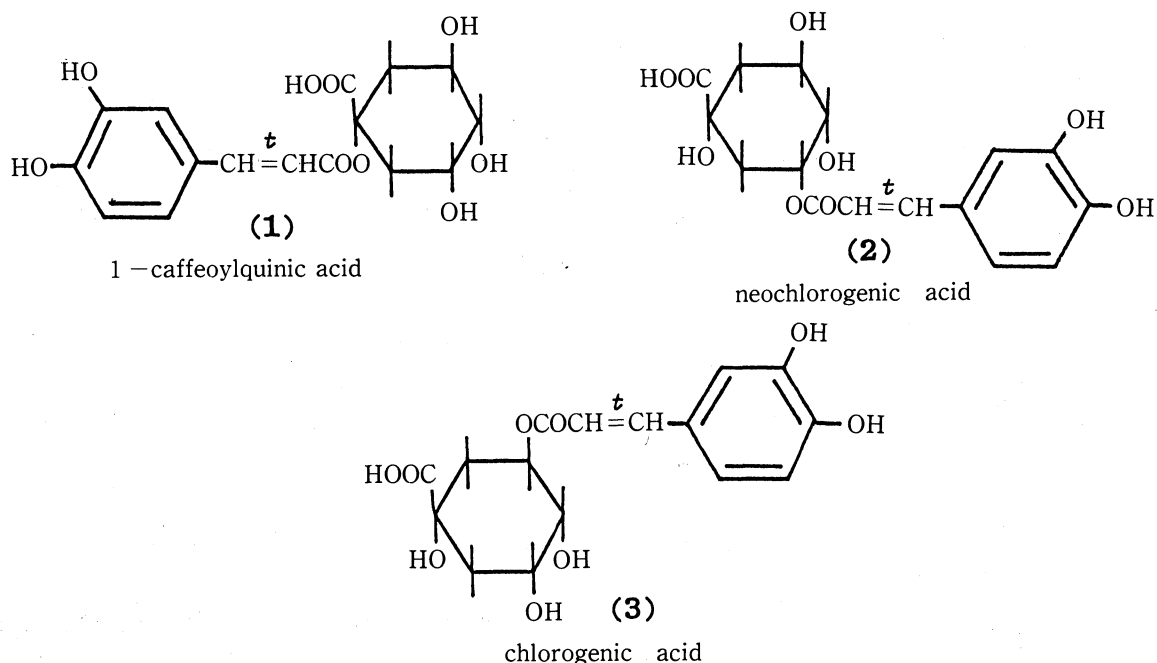
In CDCl₃

and two aromatic acetyl groups along with a caffeoyl group, three adjacent methine groups under ester oxygen and two methylene groups in analogy with **1a** (Table 1). The observed coupling constants including a W-type long range coupling showed that the configuration of a cyclohexane ring resembled that of compound **1a** except for the position of the caffeoyl group. The downfield shift of the H-5 methine signal to δ 5.34 compared to that of **1a** suggested that a caffeoyl group was attached to C-5. These observation elucidated the structure **2a**.

Compound **3a**, mp 158-159°C, showed a molecular ion at m/z 564 [M]⁺ corresponding to C₂₆H₂₈O₁₄ in the mass spectrum. The IR spectrum exhibited the presence of a carboxyl group (3000-2400 and 1720 cm⁻¹) in addition to ester (1745 cm⁻¹) and caffeoyl groups (1640 and 1500 cm⁻¹) but the absorption due to γ -lactone was not observed. The ¹H NMR spectrum showed the presence of five acetyl groups (δ 2.00, 2.08, 2.14, 2.29 and 2.30) and suggested that it resembled compounds **1a** and **2a** except for the presence of one additional acetyl group. A ¹H NMR study at 400 MHz allowed us to assign all the peaks in the spectrum as well as to drive structure **3a** except for the location of a caffeoyl group. The coupling constants of 9.6 and 3.6 Hz between three adjacent methine protons under acyloxy group at δ 5.56, 5.12 and 5.59 revealed their axial, axial and equatorial configurations. No formation of a lactone ring under acetylation suggested the configuration

of a carboxyl group to be α .

Since the original mixture of these tannins showed no absorption around 1800 cm^{-1} , both γ -lactone rings in **1a** and **2a** must have been formed during acetylation. Based on the observations, natural products **1**, **2** and **3** could be inferred to be 1-caffeoylquinic acid (**1**),⁵⁾ neochlorogenic acid (**2**)⁶⁾ and chlorogenic acid (**3**),⁷⁾ respectively. These caffeoyl tannins are rare from *Ilex* plants.



Experimental

Plant Material. The unripe fruits of *Ilex rotunda* were collected at the campus of Kagoshima University in December 1980.

Extraction and isolation. The fruits (1 kg) were extracted with MeOH. After concentration, H_2O was added and the soln was extracted with ethyl acetate and butanol. The butanol extract (4.1g) was chromatographed with MeOH on LH-20 to give a non triterpenoid fraction which was further purified by chromatography on SiO_2 to give a mixture (150 mg) of compounds **1**, **2** and **3**. The mixture was acetylated with acetic anhydride in pyridine and the product was chromatographed to give **1a** (21 mg), **2a** (36 mg) and **3a** (12 mg).

Compound 1a. Needles from MeOH; mp 177°C ; EI-MS: m/z 504 (M^+); IR (CHCl_3): 1810, 1750, 1640 and 1500 cm^{-1} ; UV (ether): 220 (ϵ 9000) and 280 nm (ϵ 13000).

Compound 2a. Colorless adhesive oil ; EI-MS : m/z 504 (M⁺) ; IR (CHCl₃) : 1810, 1750, 1640 and 1500 cm⁻¹ ; UV (ether) : 220 (ε 8500) and 280 nm (ε 12000).

Compound 3a. Needles from MeOH ; mp 158-159°C ; EI-MS : m/z 564 (M⁺) ; IR (Nujol) : 3000-2400, 1760, 1740, 1720, 1640 and 1500 cm⁻¹ ; UV (MeOH) : 219 (ε 10000) and 280 nm (ε 13000).

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References

- [1] T. Oyama, H. Aoyama, K. Yamada, T. Mitsunashi, and N. Sugiyama, *Tetrahedron Lett.* , **9**, 4639 (1968).
- [2] T. Hase, H. Hagii, M. Ishizu, M. Ochi, N. Ichikawa, and T. Kubota, *Nippon Kagaku Kaishi*, **94**, 778 (1973).
- [3] M. Nakatani, Y. Miyazaki, T. Iwashita, H. Naoki, and T. Hase, *Phytochemistry*, in press.
- [4] M. Nakatani, S. Hatanaka, H. Komura, T. Kubota, and T. Hase, *Bull. Chem. Soc. Jpn.* , in press.
- [5] V. I. Litvinenko, T. P. Popova, A. V. Simonyan, I. G. Zoz, and V. S. Sokolov, *Planta Med.* , **27**, 372 (1975).
- [6] J. Corse, *Nature*, Lond. , **172**, 771 (1953).
- [7] H. O. L. Fischer and G. Dangschat, *Ber. Dtsch. Chem. Soc.* , **72**, 4178 (1950).