Short Communication

New flavonoids from seed skin of *Xanthoceras sorbifolia*

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From ethyl acetate extract of seed skin of *Xanthoceras sorbifolia*, one compound with other known compounds was isolated by column chromatography on acetone: water: acetic acid solvent system. Structural elucidation of these compounds was carried out on the basis of Nuclear Magnetic Resonance (NMR) studies, namely ¹H-NMR, ¹³C-NMR, HMBC, HMQC and other 2D spectroscopy.

Key words: *Xanthoceras sorbifolia*, Sapindaceae, seed skin, flavonoids, epigallocatechin.

INTRODUCTION

*Xanthoceras sorbifolia* also named as *Xanthoceras sorbifolium* belongs to the family Sapindaceae. It is commonly known as yellowhorn and a member of the soapberry family and hence closely related to maples, horse-chestnuts and lychee (Chen et al., 1985). It is a kind of woody oil bearing shrub and originated primarily at Loess plateau in North of China and Inner Mongolia with characters of drought enduring, cold resistant and saline alkali enduring. The review of literature indicates the characterization of about 60 chemical constituents in the different parts of *X. sorbifolia* and belong to various classes of compounds namely saponins, coumarins and flavanoids. Earlier Bunkanka saponin A, bunkanka saponin B, bunkanka saponin C, bunkanka saponin D, 22-angeloyl-21-epoxyangeloyl barringtonenol C, 21-22-diangeloyl-24-hydroxy-R₁-barrigenol, 21,22-diangeloyl-R₁-barrigenol, Xanifolia-Y₉, Xanifolia-Y₁₂, Xanifolia-Y₁₃, Xanifolia-Y₁₇, Xanifolia-Y₁₈, Xanifolia-Y₁₀, 3-O-β-d-glucopyranosyl (1→6)-β-d-glucopyranosyl, 28-O-β-d-glucopyranosyl(1→6)-[α-L-rhamnopyranosyl (1→2)-β-d-glucopyranosyl, 16-deoxy barringtonenol C, 22-acetyl-21-O-(4-O-angeloyl)-β-d-fucopyranosyl theasapogenolB, 16-O-acetyl-21-O-(3‘, 4‘-di-O-angeloyl)-β-D-fucopyranosyl theasapogenolB, 3β,23-di hydroxy-lup-20(29)en-28-oxicacid-23-caffeate have been isolated from fruits and husks of *X. sorbifolia* (Li et al., 2005; Li et al., 2006; Chan et al., 2006; Chan et al., 2006). Saponins are widely present in *X. sorbifolia* and have been reported to possess cytotoxic activity. Its wood, bark and fruits are used to treat rheumatism, gout and enuresis of children as a folk medicine (Li et al., 2007). The mentally stimulating activity of the fruit extract has also been reported in the literature (Li et al., 1994). It has been shown that an extract from the husks of *X. sorbifolia* has cytotoxicity towards various human cancer cell lines (Chan and Mark, 2006). Since there were no reports on chemical investigation of seed skin of *X. sorbifolia*, we have carried out phytochemical investigation of seed skin.

EXPERIMENTAL

Collection and preparation of plant material

The seeds of *X. sorbifolia* were collected from China. Kernels and husks were separated manually from seeds and coarsely powdered.

Extraction of husks

Dried and powdered husks (146 g) of *X. sorbifolia* were sequentially extracted three times with methanol and distilled water at room temperature. The extracts obtained were combined and evaporated...
Figure 1. B-3’-methoxy epigallocatechin – (4β→8, 2β→O-7)-epicatechin.

Examination of methanol extract

Methanol extract was partitioned with hexane (50x3) and aqueous methanol (50x3) successively. The hexane extract (1.90 g) was column chromatographed on silica gel and nine pure compounds were isolated by repeated column chromatography, preparative TLC and HPLC. Aqueous methanol extract again partitioned with ethyl acetate, butanol and water successively.

Isolation of flavonoids

Ethyl acetate extract (380 mg) was column chromatographed on silica gel and total three compounds were isolated. Out of these two were found hydroxyl methyl esters and one compound A was obtained as brown colored solid (30.5 mg) by repeated column chromatography on acetone: water: acetic acid.

RESULTS AND DISCUSSION

Three pure compounds were isolated from ethyl acetate extract of husks by CC and HPLC. NMR data of these compounds showed that, out of three two are hydroxyl methyl esters and one compound A was found to be flavonoid. Compound A was obtained as brown colored solid (30.5 mg) by repeated column chromatography on acetone: water: acetic acid. Its $^{1}$H NMR data were same as those of procyanidin A-2 (Chan and Mark, 2006) in the region higher than 6.50 ppm. It was evident from spectral data that it is a doubly linked proanthocyanidin dimer with epigallocatechin as one of its flavan-3-ol units, whose H-B2’ and H-B6’ protons were responsible for the singlet signal observed at δ6.79. The appearance of a broad singlet due to H-F2, suggested the presence of a flavan-3-ol moiety with 2, 3-cis (epicatechin type) stereochemistry. The chemical shift of H-F2 (δ4.90) was the same as that of procyanidin (δ4.97) and obviously more downfield than that of the 4, 6-linked procyanidins A-6 and A-7 (Ma et al., 2000). Thus suggesting that the two flavan units are linked through the C-C4 and C-D8 positions. The order of the two flavan-3-ol units was determined and inter flavan linkages were confirmed by HMBC. Thus, the H-B2’, -B6’ signals of epigallocatechin at δ6.79 were correlated with the characteristic ether-linked C-C2 at δ98.3. In this manner, epigallocatechin was assigned as the upper unit and the whole structure was determined as epigallocatechin –(4β→8, 2β→O-7)-epicatechin.

$^{1}$H NMR (500 MHz, CD$_3$OD)

δ2.80 (dd, 1H-F4a), 2.97(dd, 1H-F4b), 4.06 (d, 1H-C3), 4.24(brs, 1H-F3), 4.41(d, 1H-C4), 4.90(s, 1H-F2), 6.00(d, 1H-A6), 6.06(d, 1H-A8), 6.09(s, 1H-D6), 6.79 (d, 2H-B’, B6’), 6.82(d, 1H-E5’), 7.02(dd, 1H-E6), 7.15(dd, 1H-B2’), 3.84 (OCH$_3$).

$^{13}$C NMR (500 MHz, CD$_3$OD)

δ29.3 (C-C4), 29.9 (C-F4), 67.0 (C-C3), 64.5(C-F3), 73.9 (C-F2), 96.5 (C-D6, A8), 96.7(C-A6), 98.3(C-C2), 100.2(C-D4a), 102.4(C-A4a), 104.2(C-D8), 107.3(C-B2’, B6’), 115.6 (C-E2’), 115.7 (C-E5’), 116.0 (C-E6’), 120.4(C-E1’), 131.2(C-B1’), 132.5(C-B4’), 145.7 (C-E4’), 146.0(C-B3’, E3’, B5’), 146.3(C-D8a’), 146.8(C-D5), 152.1(C-A5), 152.3(C-D7), 154.2(C-A8a), 156.6(C-A7). On the basis of the obtained spectral data, the structure of compound A was determined as B-3’-methoxy epigallocatechin –(4β→8, 2β→O-7)-epicatechin (Figure 1). Structure of compound A shows that it contains proanthocyanidin dimer with epigallocatechin. Several recent reviews have documented the importance of proanthocyanidins. These phytochemicals are widely spread throughout the plant kingdom, where they accumulate in many different organs and tissues to provide protection against predation. At the same time, they impart astringency and flavor to beverages such as wines, fruit juices and teas and are major quality factors for forage crops. They are increasingly recognized as having health beneficial effects for humans (Morimoto et al., 1987; Dixon et al., 2005). Structure elucidation of the proanthocyanidin structures in plants is important for understanding potential health beneficial effects of these dietary phytochemicals.

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REFERENCES


