Chemical Studies on *Sophora tomentosa*: the Isolation of a New Class of Isoflavonoid[1)]

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Two new pterocarpans, sophoracarpans A and B, were isolated from *Sophora tomentosa* L. (Leguminosae) in addition to three known isoflavonoids, wighteone (erythrinin B), sophoraisoflavanone A and *l*-maackiain. The structures of sophoracarpans A and B were elucidated as 6β,9-dimethoxy-3-hydroxypterocarpan and 3-hydroxy-6β-methoxy-8,9-methylenedioxypterocarpan, respectively, on the spectroscopic basis. The configurations at C-6, C-6a, and C-11a of both compounds were determined by a series of nuclear magnetic resonance irradiation experiments. The isoflavone wighteone, known as an antifungal phytoalexin in several genera of leguminous plants, was also found to occur in the genus *Sophora*.

Keywords 6-methoxypterocarpan; *Sophora tomentosa*; Leguminosae; isoflavonoid; sophoracarpan A; sophoracarpan B; stereochemistry

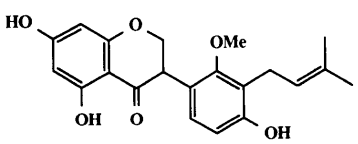
Introduction

Sophora tomentosa L. (Leguminosae) occurs very commonly along coastal areas throughout tropical Asia, extending north to the Ryukyus and Bonin Islands of Japan. This plant is of medicinal value throughout southeast Asia,[3)] *i.e.*, in eastern Malaysia, as a remedy for cholera and diarrhea, and also as an antidote after eating poisonous fish and other marine animals. In the Philippines it is regarded as an antichorelic and is a common remedy for stomach disorder. In Taiwan it has been used locally in folk medicine for the treatment of hypertension. Previous chemical investigations have mentioned the isolation of a number of flavonoids,[4-6)] including isoflavonoids, and alkaloids[7,8)] from this plant. Our further investigation on this plant has revealed the presence of two new constituents which belong to a new class of isoflavonoid.[1)] The present paper describes the isolation and characterization of the new constituents in addition to three known components.

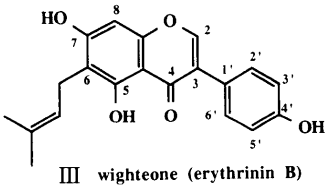
Results and Discussion

Chemical investigation of the aerial part (1.4 kg) of *S. tomentosa*, collected in the Hengchun Peninsula, Taiwan, led to the isolation of two new isoflavonoids together with three known compounds. The acetone extract was chromatographed on a silica gel column using chloroform with an increasing percentage of acetone for elution. Fractions were concentrated and monitored by thin layer chromatography (TLC) on silica gel. Fractions showing similar TLC patterns were combined and further worked up by a combination of silica gel, Sephadex LH-20 and reversed-phase silica gel column chromatographies to yield compounds I—V. Compounds I and II were readily characterized and identified as sophoraisoflavanone A and *l*-maackiain, respectively, by direct comparison with the authentic samples. These two compounds have already been isolated from the same plant by Komatsu *et al.*[5)]

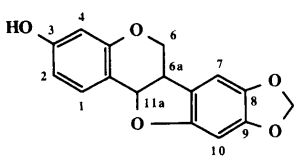
Compound III was obtained as pale yellow needles, mp 219—220 °C. The ultraviolet (UV) spectrum suggested it to be a typical isoflavone, showing an absorption maximum at 268 nm. UV shifts with sodium acetate and aluminium chloride suggested the location of A ring hydroxyl groups at C-7 and C-5 respectively. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum exhibited the presence of γ,γ-dimethylallyl group [δ 1.66, 1.78 (3H each, s), 3.35 (2H, br d, J=8 Hz) and 5.27 (1H, br t, J=8 Hz)], AA'BB' aromatic protons assignable to the B ring of compound III [δ 6.89 (2H, d, J=8.5 Hz) and 7.44 (2H, d, J=8.5 Hz)] and a characteristic proton signal at 2-position (δ 8.10). From these findings, the structure of compound III was elucidated as either 6- or 8-γ, γ-dimethylallylgenistein. The γ,γ-dimethylallyl group was found to be located at C-6 by comparison of ^{1}H- and ^{13}C-NMR chemical shifts of 8-H,



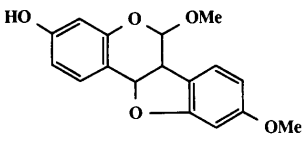
I sophoraisoflavanone A



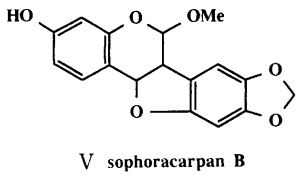
III wighteone (erythrinin B)



II *l*-maackiain



IV sophoracarpan A



V sophoracarpan B

Chart 1. Constituents Isolated from *Sophora tomentosa*

C-6 and C-8 with those of related prenyl isoflavones.[9] This isoflavone has been known as erythrinin B from *Erythrina variegata*,[10] and also as a phytoalexin or stress compound wighteone induced by fungus-innoculation or $CuCl_2$-treatment of the host plants from *Glycine wightii*,[11] several species of the genus *Lupinus*,[12-15] and several other leguminous genera.[16] The antifungal isoflavone wighteone (erythrinin B) was isolated for the first time from the genus *Sophora*.

Compounds IV and V belong to a new class of isoflavonoid, for which the new names of sophoracarpans A and B were proposed, respectively. Sophoracarpan A was obtained as optically active crystals, mp 163—165 °C, and its structure was elucidated as IV on the basis of the following evidence. The molecular formula $C_{17}H_{16}O_5$ was confirmed by high resolution mass spectroscopy. The UV and infrared (IR) spectra suggested that it is a phenolic substance devoid of carbonyl functional group. The ^{13}C-NMR spectrum closely resembles that of medicarpin,[17] a widely occurring pterocarpan, differing only in chemical shifts of C-6 and C-6a in the pterocarpan skeleton. The acetal nature of C-6 is indicated by a chemical shift of 102.6 ppm, characteristic of the acetal carbon, and a marked downfield shift (5.9 ppm) of the adjacent C-6a. The ^{1}H-NMR spectrum revealed the presence of the three resonances (δ 4.92, δ 3.62, δ 5.66) on the two hetero rings, which are assignable to 6-H, 6a-H and 11a-H, respectively. The assignments of these resonances were confirmed by ^{1}H–^{13}C selective decoupling experiments in which the irradiation of the 6-H proton at δ 4.92 collapsed the doublet C-6 signal at δ 102.6 to a sharp singlet. The orientation of a methoxy group was determined to be β by a series of irradiation experiments in which irradiating the 6a-H resulted in a substantial nuclear Overhauser effect (NOE) on the methine protons at 11a-H and 6-H (16% and 8% respectively, Fig. 1). This indicates that the methine proton (6-H) is *cis* to the neighboring methine proton (6a-H). There are two possible conformers for the pterocarpan as depicted in Fig. 2.[18] A pterocarpan with no substitution at C-6 (R = R′ = H) is in favor of conformer I based on vicinal coupling constants of related protons.[18] By contrast, 6β-methoxypterocarpan (R = H, R′ = OMe) is considered to disfavor conformer I from the stereochemical point of view, since a methoxyl group in this structure orients the axial. The magnitude of the observed coupling constants (J_{6-6a} = 5.5 Hz, J_{6a-11a} = 8.5 Hz), indicates the twisted conformation between both conformers for sophoracarpan A. The ^{1}H-NMR spectrum also reveals the presence of six protons in the aromatic proton region, which are found to be a combination of two coupling systems [ABX: δ 7.21 (dd, J = 8.4 and 0.8 Hz), 6.44 (dd, J = 8.4 and 2.3 Hz), 6.32 (d, J = 2.3 Hz), A′B′X′: δ 7.27 (d, J = 8.4 Hz), 6.56 (dd, J = 8.4 and 2.4 Hz), 6.36 (d, J = 2.4 Hz)] by spin-spin decoupling experiments. The assignment of ABX and A′B′X′ to either the A or D ring is indispensable to determine the location of an aromatic methoxyl group observed at δ 3.73. The ABX protons are finally assigned to the D-ring due to the observation of a long range coupling (0.8 Hz) between 6a-H and the signal at δ 7.21 (A). Irradiating the aromatic methoxyl furnished 9% and 13% NOE on signals at δ 6.44 (B) and δ 6.32 (X) respectively, thus confirming the location of another methoxyl on the D ring. The structure of

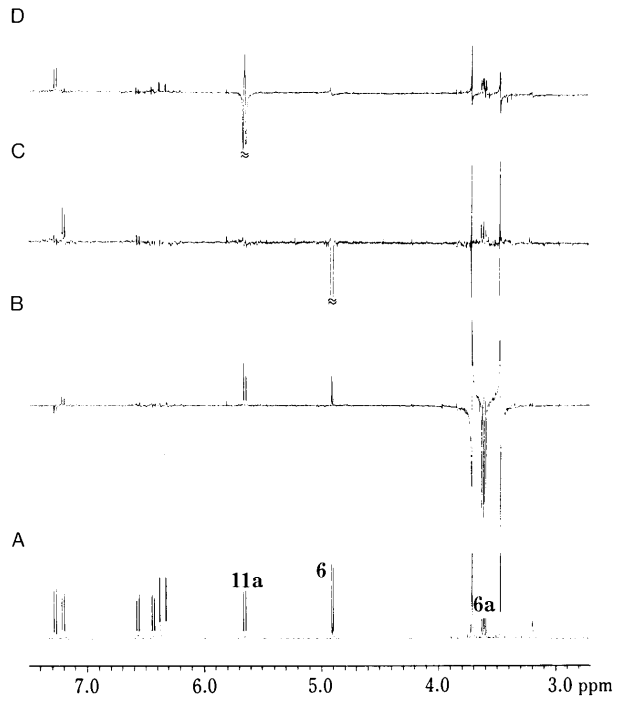


Fig. 1. NOE Difference Spectra of Sophoracarpan A

A, Reference ^{1}H-NMR spectrum; B—D, difference spectra with irradiations at δ 3.62, 4.92 and 5.66 respectively.

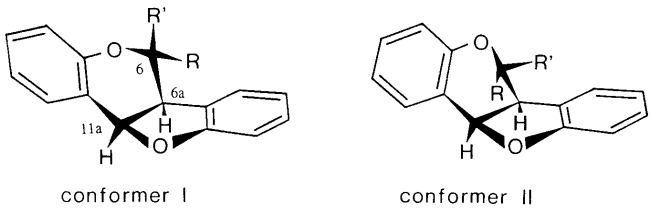


Fig. 2. Possible Conformers for the Pterocarpan

sophoracarpan A is elucidated as 6β-methoxymedicarpin (IV). Sophoracarpan B was obtained in a small amount in an amorphous form. The spectroscopic data readily depict its structure as 6β-methoxymaackiain (V).

Baruah *et al.* reported the isolation of two new 6-methoxypterocarpans from *Millettia pulchra* and established the configuration of a methoxy at C-6 as α based on the analysis of resonances attributed to the hetero rings.[19] The resonances assigned to the hetero rings of "6α-methoxyhomopterocarpin" [δ 3.56 (obsc; *sic*), 4.76 (d, J = 6.5 Hz), 5.67 (d, J = 8.5 Hz)] are in good conformity with those of sophoracarpans A and B as stated above except for their assignments. The signal at δ 4.76 was assigned to 11a-H, while the signal at δ 5.67 was assigned to 6-H in the original paper. Thus, the coupling constant between 6-H and 6a-H was put at 8.5 Hz, which led to the conclusion that the configuration of 6a-H and 6-H are assigned as *trans*. Since the assignment of these crucial resonances is unconfirmed, any discussion on the structures of 6α-methoxypterocarpin and 6α-methoxyhomopterocarpin mentioned in the original paper lacks persuasion. The authors hope that the structures of these compounds will come under review and scrutiny.

6-Methoxypterocarpan is, as mentioned above, a new class of isoflavonoid metabolites, and only four natural

compounds of this type are known thus far, including sophoracarpans A and B. Chemical investigation of *S. tomentosa* has been extensively carried out by Monache *et al.*[4] and Komatsu *et al.*,[5,6] but 6-methoxypterocarpan has been unknown from not only this plant but also other closely related taxons of the genus *Sophora*. On the other hand, Komatsu *et al.*[5] reported the isolation of 2-arylbenzofuran derivatives, which the authors have not found from this plant. In view of the biogenetic origin of 2-arylbenzofurans, their isoflavonoid nature is obvious from their structural feature, *i.e.*, the presence of a 2′-hydroxyl group, and the fact that they are of leguminous origin.[9] A biosynthesis sequence involving loss of C-6 from a coumestan, by chemical analogy with alkaline degradation of coumestans, is generally postulated for 2-arylbenzofurans, but lacks experimental proof. At this moment the role of 6-methoxypterocarpan, a newcomer to the isoflavonoid family, in the biosynthesis scheme of the isoflavonoid remains speculative. It is, however, of considerable interest to note the co-existence of a common pterocarpan, maackiain, and its 6β-methoxy form, sophoracarpan B, in the same plant since it is apparent that both compounds are closely related to 2-(2′,4′-dihydroxyphenyl)-5,6-methylenedioxy-benzofuran, which, though not found in our plant source, has been isolated from *S. tomentosa*. From the structural homology of these compounds, it is likely that a pterocarpan undergoes oxidation at C-6 followed by loss of C_1 to form 2-arylbenzofuran. Investigation on this matter is currently under way.

Experimental

All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. Spectral data were obtained using the following apparatus: ^{1}H- and ^{13}C-NMR spectra with JEOL FX-100 (^{1}H, 100 MHz; ^{13}C, 25 MHz) and Bruker AM-400 (^{1}H, 400 MHz) spectrometers with tetramethylsilane (TMS) as an internal standard; mass spectra (MS) with JEOL JMS DX-300 or D-300 mass spectrometers; IR spectra with JASCO DS-701G or JASCO FT/IR-8000 spectrometers; UV spectra with a Hitachi spectrophotometer model (100-60). Optical rotations were measured with a JASCO DIP-140 digital polarimeter. Column chromatography was carried out with the following materials; Wakogel C-200 or Kieselgel 60 (eluted with benzene–acetone or chloroform–acetone), Sephadex LH-20 (Pharmacia, eluted with MeOH) and RP-8 reversed-phase silica gel (Merck, eluted with MeOH–H_2O). TLC was conducted on a 0.25 mm precoated silica gel plate ($60F_{254}$, Merck), and spots were detected by inspection under short (254 nm) or long (360 nm) wavelength UV lights, or by the colors developed with 10% H_2SO_4 spraying followed by heating on a hot plate.

Plant Material The aerial part of *S. tomentosa* was collected in its natural habitat at Hengchun Peninsula, Taiwan, in April in 1983, and air-dried in the shade. A voucher specimen was deposited at the Herbarium of the University Museum, University of Tokyo.

Extraction and Isolation The dried aerial part (1.4 kg) of *S. tomentosa* was extracted with boiling acetone. The extract was evaporated to dryness under reduced pressure to afford a greenish-gray gum (100 g). The whole acetone extract was dissolved in acetone and adsorbed on silica gel (100 g). The adsorbed material was transfered to a silica gel column (1.5 kg, column size: i.d. 10 × 40 cm) packed in chloroform. The column was eluted with chloroform containing an increasing amount of acetone to afford a number of fractions, which were combined based upon TLC monitoring. Fractions of 500 ml were taken. The residue from fractions 19—27 (2.0 g), basically eluted with chloroform–acetone (24 : 1), was rechromatographed on silica gel (125 g, column size: i.d. 3.5 × 25 cm) with the chloroform–acetone mixture (0—100%, linear gradient) as eluents, and the volume of fractions taken was 100 ml. Fractions 24—27 (1.0 g), where pterocarpans are abundant, were combined, and subjected to a Sephadex LH-20 column chromatography (eluent: MeOH, column size: i.d. 3.3 × 29 cm). Fractions of 10 ml were taken. Fractions 17—22 afforded a pure sophoracarpan A (55 mg). The semicrystalline yellow residue (400 mg) from fractions 23—31 contained two main components, and were rechromatographed on a column of Sephadex LH-20 to give sophoracarpan B (3 mg) and *l*-maackiain (150 mg) in pure forms. Fractions 30—35 (2.2 g) eluted with chloroform–acetone (12 : 1) on the first column were separated successively by silica gel column chromatography (column size: i.d. 5 × 25 cm, eluent: benzene–acetone) followed by Sephadex LH-20 column chromatography (column size: i.d. 3.3 × 29 cm, eluent: MeOH) to afford crude sophoraisoflavanone A, and wighteone (13 mg) in a pure form. Crude sophoraisoflavanone A was purified by reversed-phase silica gel chromatography (Merck RP-8 lobar column) with MeOH–H_2O (3 : 1) as eluents to give pure sophoraisoflavanone A (200 mg).

Sophoraisoflavanone A (I) Colorless needles from benzene, mp 178—179 °C. Lit. 178—180 °C.[5] IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1600. UV λ_{max}^{MeOH} nm: 291, 330 sh. ^{1}H-NMR (100 MHz, acetone-d_6) δ: 1.67 (3H, br s, 4″-CH_3), 1.78 (3H, br s, 5″-CH_3), 3.38 (2H, br d, J=7 Hz, 1″-CH_2), 3.75 (3H, s, OCH_3), 4.26—4.55 (3H, m, 2-H_2 and 3-H), 5.29 (1H, br t, J=7 Hz, 2″-H), 5.97 (2H, s, 6- and 8-H), 6.64 (1H, d, J=8.5 Hz, 5′-H), 6.88 (1H, d, J=8.5 Hz, 6′-H), 8.0—9.0 (2H, br, 7- and 4′-OH, disappeared by the addition of D_2O), 12.30 (1H, br s, 5-OH, disappeared by the addition of D_2O). ^{13}C-NMR (25 MHz, acetone-d_6) δ: 18.1 (C-5″), 24.3 (C-1″), 25.9 (C-4″), 46.2 (C-3), 62.4 (OCH_3), 72.0 (C-2), 95.7 (C-8), 97.0 (C-6), 103.7 (C-5a), 112.1 (C-5′), 120.5 (C-3′), 122.5 (C-1′), 124.2 (C-2″), 127.9 (C-6′), 131.2 (C-3″), 156.8 (C-2′), 158.8 (C-4′), 164.3 (C-8a), 165.5 (C-5), 167.2 (C-7), 198.2 (C-4). EI-MS m/z (rel. int., %): 370 (M^+, 37), 218 (100), 163 (71), 153 (99).

***l*-Maackiain (II)** Colorless needles from MeOH–H_2O, mp 179—181.5 °C. Lit. 179—181 °C.[5] $[\alpha]_D^{22}$ −227° (c=1.0, MeOH). Lit. $[\alpha]_D$ −260°.[5] IR ν_{max}^{KBr} cm^{-1}: 3430, 1628, 1475, 1460. UV λ_{max}^{MeOH} nm: 280 sh, 286, 308. ^{1}H-NMR (100 MHz, acetone-d_6) δ: 3.52 (2H, m, 6-H_2), 4.25 (1H, m, 6a-H), 5.46 (1H, d, J=6.6 Hz, 11a-H), 5.89, 5.92 (1H each, d, J=1 Hz, –OCH_2O–), 6.35 (1H, d, J=2.5 Hz, 4-H), 6.39 (1H, s, 10-H), 6.55 (1H, dd, J=2.5, 8.5 Hz, 2-H), 6.87 (1H, s, 7-H), 7.29 (1H, d, J=8.5 Hz, 1-H), 8.60 (1H, br s, disappeared by the addition of D_2O, 3-OH). EI-MS m/z: 284 (M^+, base peak).

Wighteone (Erythrinin B) (III) Colorless prisms from MeOH–H_2O, mp 219—220 °C. UV λ_{max}^{MeOH} nm: 268; $\lambda_{max}^{MeOH+NaOAc}$ nm: 271; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 270. IR ν_{max}^{KBr} cm^{-1}: 3400, 1650. ^{1}H-NMR (100 MHz, DMSO-d_6) δ: 1.66 (3H, br s, 4″-CH_3), 1.78 (3H, br s, 5″-CH_3), 3.35 (2H, br d, J=8 Hz, 1″-CH_2), 5.27 (1H, br t, J=8 Hz, 2″-H), 6.49 (1H, s, 8-H), 6.89 (2H, d, J=8.5 Hz, 3′, 5′-H), 7.44 (2H, d, J=8.5 Hz, 2′, 6′-H), 8.10 (1H, s, 2-H), 8.65, 9.61, 13.32 (1H each, –OH, disappeared by the addition of D_2O). ^{13}C-NMR (25 MHz, DMSO-d_6) δ: 17.8 (C-5″), 21.9 (C-1″), 25.8 (C-4″), 93.6 (C-8), 105.4 (C-5a), 112.7 (C-3′ and C-5′), 122.8 (C-2″ or C-3), 123.6 (C-3 or C-2″), 130.7 (C-2′ and C-6′), 131.5 (C-3″), 153.7 (C-2), 156.5 (C-8a), 157.9 (C-5), 162.6 (C-7), 180.4 (C-4). EI-MS m/z (rel. int., %): 338 (M^+, 57), 295 (100), 283 ($M^+ - C_4H_9$), 165 (8), 118 (11), 55 (13).

Sophoracarpan A (IV) Colorless needles from MeOH–H_2O, mp 163—165 °C. $[\alpha]_D^{22}$ −110° (c=0.33, MeOH). UV λ_{max}^{MeOH} nm (log ε): 283 sh (3.89), 287 (3.92). IR ν_{max}^{KBr} cm^{-1}: 3425, 2925, 1620, 1515, 1490, 1460, 1350. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 3.47 (3H, s, 6-OCH_3), 3.62 (1H, dd, J=8.5, 5.5 Hz, 6a-H), 3.73 (3H, s, 9-OCH_3), 4.92 (1H, d, J=5.5 Hz, 6-H), 5.66 (1H, d, J=8.5 Hz, 11a-H), 6.32 (1H, d, J=2.3 Hz, 10-H), 6.36 (1H, d, J=2.4 Hz, 4-H), 6.44 (1H, dd, J=2.3, 8.4 Hz, 8-H), 6.56 (1H, dd, J=2.4, 8.4 Hz, 2-H), 7.21 (1H, dd, J=0.8, 8.4 Hz, 7-H), 7.27 (1H, d, J=8.4 Hz, 1-H), 8.52 (br s, 3-OH, disappeared by the addition of D_2O). ^{13}C-NMR (25 MHz, acetone-d_6) δ: 46.2 (C-6a), 56.1, 57.1 (OCH_3), 80.1 (C-11a), 97.3 (C-10), 102.6 (C-6), 105.0 (C-4), 107.4 (C-8), 111.2 (C-2), 114.3 (C-1a), 119.6 (C-7a), 126.7 (C-7), 132.3 (C-1), 154.4 (C-4a), 160.0 (C-3), 161.9 (C-10a), 162.4 (C-9). EI-MS m/z (rel. int., %): 300 (M^+, 21), 269 ($M^+ - OCH_3$, 30), 268 ($M^+ - CH_3OH$, base peak), 267 (93). HR-MS Calcd for $C_{17}H_{16}O_5$: 300.0995. Found: 300.0965.

Sophoracarpan B (V) Amorphous. $[\alpha]_D^{25}$ −135° (c=0.15, MeOH). UV λ_{max}^{MeOH} nm (log ε): 282 sh (3.72), 287 (3.76), 310 (3.89). ^{1}H-NMR (400 MHz, acetone-d_6) δ: 3.54 (3H, s, 6-OCH_3), 3.64 (1H, dd, J=8.5, 5.5 Hz, 6a-H), 4.98 (1H, d, J=5.5 Hz, 6-H), 5.69 (1H, d, J=8.5 Hz, 11a-H), 5.95, 5.97 (1H each, J=1.0 Hz, –OCH_2O–), 6.39 (1H, s, 10-H), 6.42 (1H, d, J=2.4 Hz, 4-H), 6.61 (1H, dd, J=2.4, 8.3 Hz, 2-H), 6.90 (1H, d, J=0.7 Hz, 7-H), 7.31 (1H, d, J=8.3 Hz, 1-H), 8.57 (1H, br s, 3-OH, disappeared by the addition of D_2O). ^{13}C-NMR (25 MHz, acetone-d_6) δ: 46.9 (C-6a), 57.2 (OCH_3), 80.1 (C-11a), 94.1 (C-10), 102.6 (C-6 and –OCH_2O–), 105.0 (C-4), 106.8 (C-7), 111.2 (C-2), 114.3 (C-1a), 118.7 (C-7a), 132.3 (C-1), 142.9 (C-8), 149.4 (C-9), 154.5 (C-10a), 155.6 (C-4a), 160.3 (C-3). EI-MS m/z (rel. int., %): 314 (M^+, 27), 283 ($M^+ - OCH_3$, 23), 282 ($M^+ - CH_3OH$, base peak), 281 (58). HR-MS Calcd for $C_{17}H_{14}O_6$: 314.0789. Found:

314.0779.

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