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Lignan, phenolic and iridoid glycosides from *Stereospermum cylindricum*

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Abstract

A lignan glycoside [(+)-cycloolivil 4′-*O*-β-D-glucopyranoside], a phenolic glycoside [3,4-dimethoxyphenyl 1-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside] and a iridoid glycoside (stereospermoside) were isolated from the leaves and branches of *Stereospermum cylindricum*, together with (+)-cycloolivil, (+)-cycloolivil 6-*O*-β-D-glucopyranoside, (−)-olivil, (−)-olivil 4-*O*-β-D-glucopyranoside, (−)-olivil 4′-*O*-β-D-glucopyranoside, vanilloloside, decaffeoyl-verbascoside, isoverbascoside, 3,4,5-trimethoxyphenyl 1-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside, ajugol, verminoside, and specioside. The structure elucidations were based on spectroscopic evidence.

Keywords: *Stereospermum cylindricum*; Bignoniaceae; Lignan glucoside; Phenolic glycoside; Iridoid glucoside; Stereospermoside

1. Introduction

As part of our systematic investigation on Thai Bignoniaceous plants, especially in tribe Tecomeae, we reported the constituents of *Fernandoa adneophylla* (Kanchanapoom et al., 2001), *Markhamia stipulata* (Kanchanapoom et al., 2002a) and *Barnettia kerrii* (Kanchanapoom et al., 2002b). To further study plants in the same tribe, we investigated the constituents of *Stereospermum cylindricum* Pierre ex P. Dop. (Thai name: Khae-Khao), collected from the Botanical garden, Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand. *S. cylindricum* is a tree up to 25 m high, distributed in South-east Asia. The bark of this plant is used in Thai traditional medicine for anti-fever purposes, as well as an anti-inflammatory agent. No phytochemical study has been carried out on this species. Preliminary studies on plants in this genus have led to isolation of several compounds such as lignans (Ghogomu et al., 1985), and quinones (Onegi et al., 2002; Kumar et al., 2003). The present paper deals with the isolation of 15 compounds, including a new lignan glycoside, a new phenolic diglycoside and a new iridoid glycoside, as well as 12 known compounds.

2. Results and discussion

The methanolic extract was suspended in H_2O and defatted with Et_2O. The aqueous layer was subjected to Diaion HP-20 column chromatography, using H_2O, MeOH and Me_2CO as eluants, successively. The portion eluted with MeOH was repeatedly subjected to silica gel, RP-18, and preparative HPLC-ODS chromatography to afford 15 compounds. Twelve were identified as (+)-cycloolivil (**1**) (Abe et al., 1988), (+)-cycloolivil 6-*O*-β-D-glucopyranoside (**2**) (Sugiyama et al., 1993), (−)-olivil (**4**) (Abe et al., 1988), (−)-olivil 4-*O*-β-D-glucopyranoside (**5**) (Abe et al., 1988), (−)-olivil 4′-*O*-*p*-glucopyranoside (**6**) (Abe et al., 1988), vanilloloside (**7**) (Ida et al., 1993), decaffeoyl-verbascoside (**8**) (Karasawa et al., 1986), isoverbascoside (**9**)

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(Kanchanapoom et al., 2002a), 3,4,5-trimethoxyphenyl 1-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside (**10**) (Kosuge et al., 1994), ajugol (**12**) (Nishimura et al., 1989), verminoside (**13**) (Sticher and Afifi-Yazar, 1979), specioside (**14**) (Compadre et al., 1982) by comparison of physical data with literature values and from spectroscopic evidence.

The molecular formula of compound **3** was determined as $C_{26}H_{34}O_{12}$ by negative ion HR-FAB mass spectrometric analysis. The ^{1}H and ^{13}C NMR spectroscopic data showed the presence of a β-glucopyranosyl unit from the anomeric proton signal at δ_H 4.83 (*d*, $J = 7.3$ Hz) and from the carbon signals at δ_C 102.9, 78.1, 77.8, 74,9, 71.3 and 62.5, in addition to the signals of the aglycone moiety. The chemical shifts of the aglycone moiety were similar to those of (+)-cycloolivil (**1**), suggesting that compound **3** is (+)-cycloolivil glucoside. This was supported by enzymatic hydrolysis of **3** with crude hesperidinase, providing compound **1**. The location of the sugar unit was assigned by an NOESY experiment, in which NOESY correlation was found between δ_H 4.83 (*d*, $J = 7.3$ Hz, H-1″) and δ_H 7.08 (*d*, $J = 8.3$ Hz, H-5′), indicating that the sugar part was attached at C-4′. Moreover, HMBC spectrum provided the further confirmation of the structure from the three-bond correlation between H-1″ (δ_H 4.83) and C-4′ (δ_C 146.6) as illustrated in Fig. 1. Therefore, structure of compound **3** was elucidated as (+)-cycloolivil 4′-*O*-β-D-glucopyranoside.

The molecular formula of compound **11** was determined as $C_{19}H_{28}O_{12}$ by negative ion HR-FAB mass spectrometric analysis. The ^{1}H NMR spectrum indicated the presence of a tri-substituted aromatic ring (ABX system) from the signals at δ_H 6.83 (*d*, $J = 8.8$ Hz), 6.64 (*d*, $J = 2.1$ Hz) and 6.59 (*dd*, $J = 8.8$, 2.7 Hz), two singlet methoxyl signals at δ_H 3.72 and 3.68, and two anomeric proton signals at δ_H 4.69 (*d*, $J = 7.6$ Hz) and 4.16 (*d*, $J = 7.3$ Hz). The ^{13}C NMR spectrum displayed 19 carbon signals, of which three were assignable to three oxy-aryl carbons at δ_C 151.9, 149.3 and 144.0, three aryl-methines at δ_C 112.8, 107.3 and 102.3, and two methoxyl groups at δ_C 56.1 and 55.5 for the aglycone moiety. The remaining carbon signals belonged to the sugar moiety, and could be identified as β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranosyl unit by comparing chemical shifts with those of 3,4,5-trimethoxyphenyl 1-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside (**10**). All protonated carbons were assigned by the result from HSQC spectrum. From these spectral data, compound **11** is a glycoside of dimethoxylphenol. The locations of two methoxyl groups and the sugar moiety were assigned by NOESY experiment The significant correlations observed between the signals were at: (i) δ_H 4.69 (H-1′) and δ_H 6.64 (H-2), (ii) δ_H 4.69 (H-1′) and δ_H 6.59 (H-6), (iii) δ_H 6.64 (H-2) and δ_H 3.72 (MeO-3), and (iv) δ_H 6.83 (H-5) and δ_H 3.68 (MeO-4); indicating that two methoxyl groups were attached at C-3 and C-4, as well as the sugar moiety was substituted at C-1. Consequently, the structure of compound **11** was identified to be 3,4-dimethoxyphenyl 1-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside.

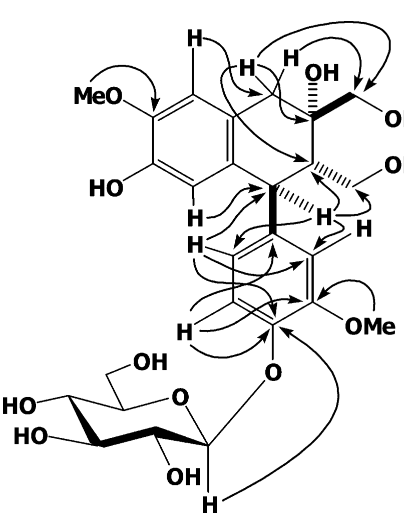
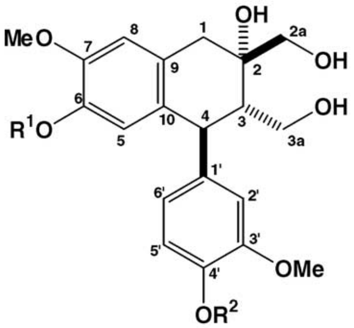


Fig. 1. Significant HMBC correlations of compound **3**.

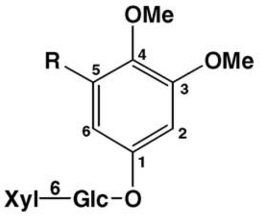
The molecular formula of compound **15** was determined as $C_{24}H_{30}O_{13}$ negative ion HR-FAB mass spectrometric analysis. The ^{13}C NMR spectroscopic data showed the presence of one β-glucopyranosyl unit, one coumaroyl moiety in addition to nine carbons signal for the aglycone moiety. DEPT experiments indicated that compound **15** contained one quarternary carbinolic carbon (δ_C 80.7), seven methines (δ_C 140.8, 106.0, 93.0, 85.8, 84.3, 48.3 and 36.5) and one methylene (δ_C 64.3) for the aglycone part, consistent with cyclopentanopyran ring of an iridoid skeleton. The chemical shift at δ_C 93.0 was characteristic of an acetal group of C-l. The methine signals at δ_C 140.8 and 106.0 were assigned to a disubstituted olefin group at C-3 and C-4, respectively. The coumaroyl moiety was assigned as *trans* by the coupling constant of the proton signals at δ_H 7.60 and 6.32 (each *d*, $J = 15.9$ Hz). The remaining signals in the ^{1}H NMR spectrum at δ_H 5.50 (*d*, $J = 4.4$ Hz), 6.22 (*dd*, $J = 6.1$, 1.8 Hz), 5.19 (*dd*, $J = 6.1$, 3.4 Hz), 2.71 (*m*), 4.71 (*dd*, $J = 5.6$, 5.4 Hz), 4.09 (*d*, $J = 5.6$ Hz), and 2.45 (*dd*, $J = 9.8$, 4.4 Hz) were assignable to H-1, H-3, H-4, H-5, H-6, H-7 and H-9, respectively. Also, it showed the AB type of methylene protons at δ_H 3.98 and 3.78 (each *d*, $J = 12.0$ Hz), ascribable to H-10. The ^{1}H and ^{13}C NMR spectroscopic data were closely related to those of decinnamoyl-globularimin (**16**) (Chaudhuri and Sticher, 1981), except for a set of additional signals arising from the coumaroyl moiety. This ester moiety was assigned to be located at C-6 since the chemical shifts of C-6, C-5 and C-7 were significantly changed by +2.7, −0.8, and −2.1 ppm, respectively. Moreover, the HMBC spectrum (Fig. 2.) provided further confirmation from the three-bond correlation from H-6 (δ_H 4.71) to C-9″ (δ_C 169.1). Therefore, the structure of compound **15** was determined as 6-*O*-*trans*-*p*-coumaroyl-decinnamoyl-globularimin, namely stereospermoside.



1 : R^1 = R^2 = H

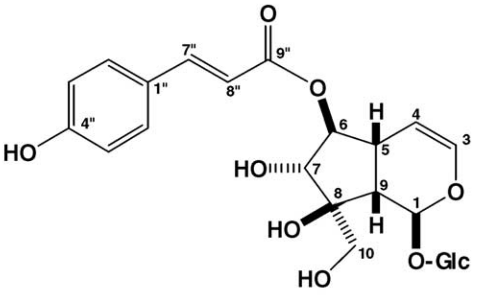
2 : R^1 = Glc, R^2 = H

3 : R^1 = H, R^2 = Glc

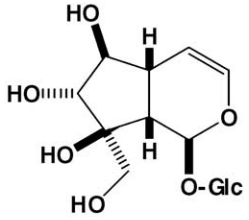


10 : R = OMe

11 : R = H



15



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Among the compounds isolated, the present study yielded two phenylethanoid glycosides (**8**–**9**) and four iridoid glucosides (**12**–**15**). The phenylethanoid glycosides, decaffeoyl-verbascoside (**8**) and isoverbascoside (**9**), are widely distributed in Bignoniaceous plants, such as in Thailand (Kanchanapoom et al., 2001, 2002a,b). Iridoids are also widespread in the family Bignoniaceae (von Poser et al., 2000), especially those lacking a carboxylic acid functionality at C-4. These appears to be the most common for tribe Tecomeae such as ajugol (**12**), verminoside (**13**), specioside (**14**), and stereospermoside (**15**). Thus, these two classes of compounds may serve as useful chemotaxonomical methods in tribe Tecomeae of the family Bignoniaceae.

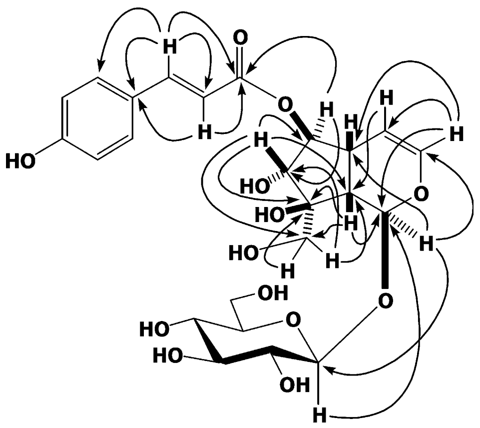

Fig. 2. Significant HMBC correlations of compound **15**.

3. Experimental

3.1. General

^{1}H, ^{13}C and 2D NMR spectra were recorded using a JEOL JNM α-400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). The NMR spectroscopic data were measured in CD3OD and DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The negative-ion mode FAB-MS spectra were recorded on a JEOL JMS-SX 102 spectrometer. IR spectra were measured with a Perkin Elmer Spectrum one FT-IR spectrometer. Optical rotations were determined on a Union PM-1 digital polarimeter. For column chromatography, silica gel G (Merck no. 7734), YMC-gel ODS (50 μm, YMC) and highly porous copolymer resin of styrene and divinylbenzene (Mitsubishi Chem. Ind. Co. Ltd.) were used. HPLC (Jasco PU-980 pump) were carried on columns of ODS (150 × 20 mm i.d., YMC) and Polyamine II (250 × 4.6 mm i.d.) with a Toyo Soda refractive index (RI-8000) detector. The flow rate was 6 ml/min. The solvent systems were (I) EtOAc–MeOH (9:1), (II) EtOAc–MeOH–H_2O (40:10:1), (III) EtOAc–MeOH–H_2O (70:30:3), (IV) 10–50% aqueous MeOH, (V) 10% aqueous MeCN, (VI) 12% aqueous MeCN, (VII) 15% aqueous MeCN, (VIII) 20% aqueous MeCN, (IX) 20% aqueous MeOH and (X) 80% aqueous MeCN, respectively.

3.2. Plant material

The leaves and branches of *S. cylindricum* Pierre ex. P. Dop were collected from Botanical Garden, Faculty of Pharmaceutical Sciences, Khon Kaen University in July, 2004, and identified by Mr. Bamrung Tavinchiua of the Department of Pharmaceutical Botany and Pharmacognosy, Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand. A voucher sample (PSKKU-0050) is kept in the Herbarium of the Faculty of Pharmaceutical Sciences, Khon Kaen University, Thailand.

3.3. Extraction and isolation

Dried leaves and branches (2.5 kg) of *S. Cylindricum* were extracted with hot MeOH three times/(under reflux, 5 l, for each extraction). After removal of the solvent by evaporation, with Et_2O. The aqueous layer was applied to a column of Diaion HP-20 and eluted successively with H_2O, MeOH and Me_2O. The fraction eluted with MeOH (49.3 g) was subjected to a silica gel cc using solvent systems I (2.0 l), II (5.0 l) and III (4.0 l). Five fractions were collected. Fraction 2 (5.1 g) was located onto a column of RP-18 using solvent system IV to provide compounds **1** (1.23 g) and **4** (519.9 mg). Fraction 3 (18.9 g) was applied to a RP-18 column using solvent system IV, affording 12 fractions. Fraction 3–1 was purified by preparative HPLC-ODS with solvent system V to give compounds **7** (195.6 mg), **8** (154.8 mg) and **12** (36.4 mg). Fraction 3–3 was purified by preparative HPLC-ODS with solvent system VII to obtain compounds **5** (353.8 mg) and **6** (92.3 mg). Fraction 3–5 was further purified by preparative HPLC-ODS with solvent system VIII to afford compounds **9** (68.8 mg), **13** (627.5 mg) and **15** (49.2 mg). Compound **14** (430.0 mg) was crystallized from fractions 3–7 and 3–8. Fraction 4 (15.4 mg) was similarly separated on a column of RP-18 using solvent system IV to give eight fractions. Fraction 4–3 was purified by preparative HPLC-ODS with solvent system VI to give compound **10** (135.4 mg) and fraction 4-3-2. This fraction was further purified by preparative HPLC-ODS with solvent system IX to give compound **2** (54.2 mg) and fraction 4-3-2-2, which was finally purified by analytical HPLC-Polyamine II with solvent system X to provide compounds **3** (26.3 mg) and **11** (13.7 mg).

*3.4. (+)-Cycloolivil-4′-O-β-D-glucopyranoside (**3**)*

Amorphous powder, $[\alpha]_D^{24}$ +17.6 (MeOH, *c* 1.59); IR ν_{max}^{KBR} cm^{-1}: 3434, 2920, 1617, 1514, 764; for ^1H and ^{13}C NMR (CD_3OD) spectra, see Table 1; negative HR-FAB-MS, *m/z*: 537.1967 $[M - H]^-$ (calcd for $C_{26}H_{33}O_{12}$, 537.1972).

*3.5. Enzymatic hydrolysis of compound **3***

Compound **3** (13.0 mg) was hydrolyzed with crude hesperidinase (25 mg) in 2 ml of H_2O. After stirring at 37 °C for 24 h, the reaction mixture was extracted with EtOAc, and then evaporated to dryness to provide (+)-cycloolivil (5.2 mg), $[\alpha]_D^{24}$ +85.4), whose structure was identified using physical and NMR spectral analyses.

*3.6. 3,4-Dimethoxyphenyl 1-O-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside (**11**)*

Amorphous powder, $[\alpha]_D^{24}$ −100.7 (DMSO, *c* 0.45); IR ν_{max}^{KBr} cm^{-1}: 3533, 3380, 3275, 2921, 1602, 1522, 833; for ^1H and ^{13}C NMR (DMSO-d_6) spectra, see Table 2; negative HR-FAB-MS, *m/z*: 447.1477 $[M - H]^-$ (calcd for $C_{19}H_{27}O_{12}$ 447.1503).

Table 1
NMR Spectroscopic data of compound **3**

No.	δ_C	δ_H
1	39.9	3.17 (1H, *d*, *J* = 16.8 Hz) 2.57 (1H, *d*, *J* = 16.8 Hz)
2	74.9	
2a	69.3	3.75 (1H)[a] 3.55 (1H, *d*, *J* = 11.2 Hz)
3	47.5	2.00 (1H, *br d*, *J* = 11.5 Hz)
3a	60.8	3.75 (1H)[a] 3.49 (1H, *dd*, *J* = 11.2, 4.2 Hz)
4	45.0	4.03 (1H, *br d*, *J* = 11.5 Hz)
5	117.3	6.11 (1H, *s*)
6	145.4	
7	147.6	
8	113.0	6.59 (1H, *s*)
9	133.1	
10	126.5	
MeO-7	56.7	3.75 (3H, *s*)
MeO-3′	56.4	3.74 (3H, *s*)
1′	142.0	
2′	114.9	6.75 (1H, *d*, *J* = 1.9 Hz)
3′	150.8	
4′	146.6	
5′	117.9	7.08 (1H, *d*, *J* = 8.3 Hz)
6′	123.6	6.72 (1H, *dd*, *J* = 8.3, 1.9 Hz)
1″	102.9	4.83(1H, *d*, *J* = 7.3 Hz)
2″	74.9	3.43 (1H, *dd*, *J* = 8.3, 7.3 Hz)
3″	77.8	3.42 (1H, *dd*, *J* = 9.0, 8.3 Hz)
4″	71.3	3.36 (1H, *dd*, *J* = 9.0, 8.3 Hz)
5″	78.1	3.26 (1H, *m*)
6″	62.5	3.84 (1H, *br d*, *J* = 12.0 Hz) 3.65 (1H, *dd*, *J* = 12.0, 5.6 Hz)

[a] Chemical shifts obtained approximately by HSQC.

Table 2
NMR Spectroscopic data of compound **11** (DMSO-d_6)

No.	δ_C	δ_H
1	151.9	
2	102.3	6.64 (1*H*, *d*, *J* = 2.7 Hz)
3	149.3	
4	144.0	
5	112.8	6.83 (1H, *d*, *J* = 8.8 Hz)
6	107.3	6.59 (1H, *d*, *J* = 8.8, 2.7 Hz)
MeO-3	55.5	3.72 (3H, *s*)
MeO-4	56.1	3.68 (3H, *s*)
1′	101.2	4.69 (1H, *d*, *J* = 7.6 Hz)
2′	73.2	3.21 (1H)[a]
3′	76.5	3.22 (1H)[a]
4′	69.8	3.11 (1H, *dd*, *J* = 9.0, 8.1 Hz)
5′	75.9	3.45 (1H, *m*)
6′	68.5	3.93 (1H, *br d*, *J* = 11.0 Hz) 3.56 (1H, *dd*, *J* = 11.0, 6.6 Hz)
1″	103.9	4.16 (1H, *d*, *J* = 7.3 Hz)
2″	73.4	2.94 (1H, *dd*, *J* = 8.8, 7.3 Hz)
3″	76.6	3.05 (1H, *d*, *J* = 8.8, 8.5 Hz)
4″	69.6	3.25 (1H, *m*)
5″	65.7	3.65 (1H, *dd*, *J* = 11.2, 5.1 Hz) 2.95 (1H, *dd*, *J* = 11.2, 3.9 Hz)

[a] Chemical shifts obtained approximately by HSQC.

Table 3
NMR Spectroscopic data of compound **15**

No.	δ_C	δ_H
1	93.0	5.50 (1H, *d*, $J = 4.4$ Hz)
3	140.8	6.22 (1H, *dd*, $J = 6.1$, 1.8 Hz)
4	106.0	5.19 (1H, *dd*, $J = 6.1$, 3.4 Hz)
5	36.5	2.71 (1H, *m*)
6	85.8	4.71 (1H, *dd*, $J = 5.6$, 5.4 Hz)
7	84.3	4.09 (1H, *d*, $J = 5.6$ Hz)
8	80.7	
9	48.3	2.45 (1H, *dd*, $J = 9.8$, 4.4 Hz)
10	64.3	3.98 (1H, *d*, $J = 12.0$ Hz) 3.78 (1H, *d*, $J = 12.0$ Hz)
1′	99.5	4.62 (1H, *d*, $J = 7.8$ Hz)
2′	74.7	3.16 (1H, *dd*, $J = 8.8$, 7.8 Hz)
3′	77.9	3.22 (1H, *dd*, $J = 9.0$, 8.8 Hz)
4′	71.6	3.26 (1H, *dd*, $J = 9.0$, 8.0 Hz)
5′	78.1	3.27 (1H, *m*)
6′	62.8	3.83(1H, *br d*, $J = 11.7$ Hz) 3.62 (1H, *dd*, $J = 11.7$, 3.9 Hz)
1″	127.1	
2″, 6″	131.2	7.41 (2H, *d*, $J = 8.8$ Hz)
3″, 5″	116.8	6.76 (2H, *d*, $J = 8.8$ Hz)
4″	161.3	
7″	146.9	7.60 (1H, *d*, $J = 15.9$ Hz)
8″	115.0	6.32 (1H, *d*, $J = 15.9$ Hz)
9″	169.1	

3.7. Stereospermoside (*15*)

Amorphous powder, $[\alpha]_D^{24}$ −90.8 (MeOH, *c* 1.74); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3427, 2927, 1692, 1605, 832; for ^{1}H and ^{13}C NMR (CD_3OD) spectra, see Table 3; negative HR-FAB-MS, *m*/*z*: 525.1599 $[M - H]^-$ (calcd for $C_{24}H_{29}O_{13}$, 525.1608).

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