Studies on Monoterpene Glucosides. VIII.¹⁾ Artefacts formed during Extraction of Asperuloside and Paederoside

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Prolonged boiling of an aqueous solution of asperuloside (I) afforded scandoside (III), deacetylasperuloside (V), deacetylasperulosidic acid (IX), 10-acetylscandoside (X), and asperulosidic acid (XI). A methanolic solution of I gave deacetylasperuloside (V) and daphylloside (XII) on the same treatment.

Prolonged boiling of an aqueous solution of paederoside (II) gave paederosidic acid (IV) and 6-epipaederosidic acid (XIII). Deacetylasperuloside (V) and paederosidic acid methyl ester (VI) were obtained by boiling a methanolic solution of II.

As mentioned in the preceding paper, paper chromatographic analysis of an aqueous extract obtained by boiling fresh leaves of *Paederia scandens* (LOUR.) MERRILL var. *mairai* (Léveillé) HARA with water for 15 minutes demonstrated only three iridoid glucosides: asperuloside (I), paederoside (II) and scandoside (III). Besides these substances, paederosidic acid (IV) and deacetylasperuloside (V) were also isolated from aqueous extracts of this plant. The methanolic extract of the plant, however, did not contain paederosidic acid (IV) although it contained a small amount of a substance whose NMR spectrum suggested it to be paederosidic acid methyl ester (VI). Thus IV and V seem to be artefacts while I, II and III are the intrinsic glucosides of this plant.

This paper is on the products formed by boiling glucosides (I) and (II) in water or methanol which were examined to find out whether substances like IV or V were actually formed during the extraction.

An aqueous solution of asperuloside (I) was first heated in a boiling water bath for 10 hours and then analysed by counter-current distribution, using as solvent *n*-butanol-pyridine-water (10:1:10 v/v) (solvent system 1). The distribution curve is shown in Fig. 1a. Asperuloside (I) was recovered from the fraction in tubes 121—191. The fraction in tubes 62—106 gave a white powder, $C_{16}H_{20}O_{10} \cdot 2H_2O$, mp 118—120°, $[\alpha]_D^{25} -119.4^\circ$, which was identified as deacetylasperuloside (V) by comparison of its ultraviolet (UV), infrared (IR) and nuclear magnetic resonance (NMR) spectra with those of authentic material.

The fraction in tubes 1—61 was redistributed in a solvent system consisting of *n*-butanol-ethanol-water (10:1:10 v/v) (solvent system 2) to give the distribution curve shown in Fig. 1b. Although the NMR spectrum of the white powder obtained from the fraction in tubes 1—26 was similar to that of scandoside (III), the signal for the C-1 proton was in a higher field appearing at 4.82 τ . As the IR spectrum showed absorption maxima at 1540 and 1400 cm^{-1} , presumably due to a carboxylate group, besides an enolether band at 1640 cm^{-1} , the substance seemed to be a salt of scandoside (III). Acetylation of compound (III) by the usual method furnished a hexaacetate (VII), which was then methylated to give hexaacetate methyl ester, $C_{29}H_{36}O_{17}$, mp 131—133°. This compound was found to be identical with an authentic

1) Part VII: H. Inoue, S. Inoue, N. Shimokawa, and M. Okigawa, *Chem. Pharm. Bull.* (Tokyo), **17**, 1942 (1969).

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specimen of scandoside hexaacetate methyl ester (VIII). Thus the original compound should be a salt of scandoside (III), though its cation is still unknown.

The NMR spectrum of the white powder obtained from the fraction in tubes 62—91 showed that it was a mixture of two parts of deacetylasperulosidic acid (IX) and one part of scandoside (III) but it has not yet been studied in detail. The fraction in tubes 117—156 afforded a substance (X), $C_{18}H_{24}O_{12} \cdot H_2O$, mp 133—137°, giving NMR signals at 2.47 τ (1H, d, $J=1$ cps, C-3), 4.06 τ (1H, m, C-7), 4.64 τ (1H, d, $J=5$ cps, C-1), 5.15 τ (2H, m, C-10), 6.55 τ

Fig. 1a. Separation of Asperuloside (I) and Deacetylasperuloside (V) by Counter-current Distribution

solvent system 1

transfers 549

Fig. 1b. Separation of Scandoside (III), Deacetylasperulosidic Acid (IX), 10-Acetylscandoside (X) and Asperulosidic Acid (XI) by Counter-current Distribution

solvent system 2

transfers 679

- I : $R_1 = CH_3CO_2$, $R_2 = H$
 II : $R_1 = CH_3COS$, $R_2 = H$
 V : $R_1 = HO$, $R_2 = H$

- III : $R_1 = R_2 = R_3 = R_4 = H$
 VII : $R_1 = R_2 = R_3 = CH_3CO$, $R_4 = H$
 VIII : $R_1 = R_2 = R_3 = CH_3CO$, $R_4 = CH_3$
 X : $R_1 = R_3 = R_4 = H$, $R_2 = CH_3CO$

- IX : $R_1 = R_2 = R_3 = H$
 XI : $R_1 = CH_3CO$, $R_2 = R_3 = H$
 XII : $R_1 = R_3 = H$, $R_2 = CH_3$

- IV : $R_1 = HO$, $R_2 = R_3 = H$
 XIII : $R_1 = R_3 = H$, $R_2 = HO$

(3H, C-5, C-6'), 6.84 τ (1H, C-9), and 7.85 τ (3H, s, CH_3COO-). The spectrum is very similar to that of scandoside (III) except for the presence of an acetoxy signal and a down field shift of its signal due to the C-10 protons. Acetylation of this compound (X) by the usual method followed by methylation furnished a pentaacetate methyl ester, $C_{29}H_{36}O_{17}$, mp 133—135°, which was found to be identical with VIII. Thus the original substance (X) is 10-acetylscandoside.

The fraction in tubes 167—216 afforded a white powder (XI) with mp 127—131° and analytic values corresponding to $C_{18}H_{24}O_{12} \cdot 2H_2O$. The NMR spectrum of XI showed signals at 2.30 τ (1H, d, $J=1$ cps, C-3), 3.89 τ (1H, m, C-7), 6.89 τ (1H, t, C-9), and 7.25 τ (1H, t, C-5) which are characteristic of those of deacetylasperulosidic acid (IX). However, its spectrum differs from that of IX in having an extra singlet due to an acetyl group at 7.85 τ and a shift of 0.51 ppm to the lower field of 5.09 τ of the signal due to the C-10 protons. Accordingly this substance seems to have structure XI, which could be obtained by opening the lactone ring of asperuloside (I) and it was designated as asperulosidic acid.

A methanolic solution of asperuloside (I) was then refluxed for 50 hours and the reaction mixture was subjected to counter-current distribution with solvent system 2 to give the distribution pattern shown in Fig. 2. The fraction in tubes 65—85 furnished a white powder, mp 117—118°, with IR and NMR spectra indicating it was deacetylasperuloside (V). Asperuloside (I) was recovered from the fraction in tubes 120—140. The fraction in tubes 175—200 gave a white powder, $C_{19}H_{26}O_{12} \cdot H_2O$, mp 99—101°, $[\alpha]_D^{20} +18.3^\circ$ (H_2O), which had identical NMR and IR spectra to daphylloside³⁾ (XII).

Fig. 2. Separation of Asperuloside (I), Deacetylasperuloside (V) and Daphylloside (XII) by Counter-current Distribution

solvent system 2 transfers 450

Fig. 3a. Separation of Paederoside (II) by Counter-current Distribution

solvent system 1 transfers 340

Fig. 3b. Separation of Paederosidic Acid (IV) and 6-Epipaederosidic Acid (XIII) by Counter-current Distribution

solvent system 2 transfers 347

Fig. 4. Separation of Paederoside (II), Deacetylasperuloside (V) and Paederosidic Acid Methylester (VI) by Counter-current Distribution

solvent system 2 transfers 357

An aqueous solution of paederoside (II) was boiled for 10 hours and on counter-current distribution employing solvent system 1 the reaction product gave the distribution curve shown in Fig. 3a. Paederoside (II) was recovered from the fraction in tubes 201—261. The

3) H. Inouye, S. Ueda, M. Hirabayashi and N. Shimokawa, *Yakugaku Zasshi*, **86**, 943 (1966).

fraction in tubes 31—76 was redistributed in solvent system 2 to give the distribution curve shown in Fig. 3b. The fraction in tubes 201—231 afforded a white powder, $C_{18}H_{24}O_{11}S \cdot 2H_2O$, mp 124—129°, $[\alpha]_D^{25} +54.4^\circ$ (MeOH), with an NMR spectrum superimposable upon that of paederosidic acid (IV). The fraction in tubes 156—181 gave a white powder, $C_{18}H_{24}O_{11}S \cdot 2H_2O$, mp 85—91°, $[\alpha]_D^{25} +26.4^\circ$, with an NMR spectrum similar to that of 10-acetylscandoside except for the shift of the signal of the acetoxyl group of the former by 0.18 ppm to 7.67 τ and of the C-10 protons by 0.15 ppm to 5.00 τ . These data suggest that the substance should be 6-epipaederosidic acid (XIII).

A methanolic solution of paederoside (II) was refluxed for 100 hours and the resulting reaction mixture was subjected to counter-current distribution with solvent system 2 to give the distribution pattern shown in Fig. 4. The substance obtained from the fraction in tubes 101—140 seemed to be deacetylasperuloside (V) from its IR spectrum but further examination was impossible because of the small amount of sample available. Paederoside (II) was recovered from the fraction in tubes 216—271. The fraction in tubes 276—300 afforded a white powder, $C_{19}H_{26}O_{11}S \cdot 2H_2O$, mp 85—89°, $[\alpha]_D^{25} +16.8^\circ$. The NMR signals of this compound appeared at 2.29 τ (1H, d, $J=1$ cps, C-3), 3.87 τ (1H, m, C-7), 4.94 τ (2H, m, C-10), 6.22 τ (3H, s, $-COOCH_3$) and 7.62 τ (3H, s, CH_3COS-). Besides these signals, two triplets for the protons at C-5 and C-9 appeared at 6.89 τ and 7.29 τ , respectively, which are characteristic of daphylloside (XII), deacetylasperulosidic acid (IX) and paederosidic acid (IV). Thus this substance seems to be paederosidic acid methyl ester (VI).

Thus when an aqueous or methanolic solution of asperuloside (I) or paederoside (II) is refluxed the lactone ring or the acetyl ester linkage undergoes hydrolysis or methanolysis to afford several decomposition products. The formation of IV, V and VI by this treatment suggests that in the work described in the previous paper these substances were formed during extraction of material from plant tissue.

The fact that daphylloside (XII) was formed by methanolysis of asperuloside (I) coupled with the experimental result that asperuloside (I) was only a detectable iridoid glucoside on a paper chromatogram of an extract of *Daphniphyllum macropodum* MIQ. obtained by boiling the fresh leaves of the plant with methanol suggests that this glucoside is probably also an artefact. The formation of a small amount of the C-6 epimer by hydrolysis of I or II is reasonable because the C-6 hydroxyl group is located at an allylic position.

Experimental⁴⁾

Effect of Boiling an Aqueous Solution of Asperuloside (I)—One g of I was dissolved in 30 ml of H_2O and the solution was heated on a boiling water bath for 10 hr. After cooling, the resulting dark brown precipitate was filtered off and washed with a little H_2O . The washing water was combined with the filtrate and concentrated *in vacuo*. The resulting syrupy residue was dissolved in *ca.* 10 ml of the H_2O layer and subjected to the counter-current distribution under the conditions shown in Fig. 1a. The fraction in tubes 121—191 was concentrated *in vacuo* to recover 360 mg of asperuloside (I). PPC: *Rf* (A) 0.44, (B) 0.45, (C) 0.49.

The syrupy residue obtained by concentration of the fraction in tubes 62—106 *in vacuo* was dissolved in MeOH and passed through a short charcoal column with the same solvent as eluent. The eluate was concentrated *in vacuo* to give a colorless syrupy residue. It was dissolved in H_2O and lyophilized to give 33 mg of a slightly brown powder. This substance was rechromatographed on charcoal and lyophilized to give pure deacetylasperuloside (V), mp 118—120°, $[\alpha]_D^{25} -119.4^\circ$ ($c=0.50$, MeOH), UV λ_{max}^{EtOH} m μ (log ϵ):

4) NMR spectra were determined on a Varian A-60 high resolution NMR spectrometer in D_2O with DSS and in other solvents with TMS as an internal standard. All melting points are given as uncorrected values. Paper chromatography (PPC) was carried out on Toyo Roshi No. 50 filter paper with the upper layer of the following solvent systems. (A) *n*-BuOH-EtOH- H_2O (4:1:5 v/v), (B) *n*-BuOH-pyridine- H_2O (4:1:5 v/v), (C) *n*-BuOH-AcOH- H_2O (4:1:5 v/v). Iridoid glucosides were detected as described in the preceding paper. Counter-current distribution was also performed as described in the preceding paper.

238 (3.78). The IR and NMR spectra were identical with those of authentic material. PPC: *Rf* (A) 0.28, (B) 0.37, (C) 0.28. *Anal.* Calcd. for $C_{16}H_{20}O_{10} \cdot 2H_2O$: C, 47.06; H, 5.92. Found: C, 47.04; H, 6.36.

The fraction in tubes 1—61 was concentrated *in vacuo*. The resulting syrup was dissolved in *ca.* 10 ml of the H_2O layer and subjected to counter-current-distribution under the conditions shown in Fig. 1b. The fraction in tubes 1—26 was concentrated *in vacuo* to give an oily residue, which was dissolved in MeOH and treated with charcoal (by column chromatography), and the solvent was removed *in vacuo*. The residue was dissolved in H_2O and lyophilized to give 31 mg of a white powder. This substance was allowed to stand overnight with 0.3 ml each of pyridine and Ac_2O . The reaction mixture was then poured into ice water. The resulting syrup was dissolved in MeOH and after the treatment with charcoal, the solvent was removed *in vacuo* to yield 33 mg of a syrupy residue. The NMR spectrum of this substance was in good accordance with that of scandoside hexaacetate (VII). The acetate (33 mg) was dissolved in ether and allowed to stand with CH_2N_2 -ether solution. After removal of ether, the resulting syrup was taken up in ether and chromatographed over Al_2O_3 (5 g) with ether as eluent. The eluate was concentrated and the residue was recrystallized from ether to afford 9 mg of colorless needles, mp 131—133°. This substance was shown to be identical with a specimen of VIII by comparison of the IR spectra and by the mixed melting point. *Anal.* Calcd. for $C_{29}H_{36}O_{17}$: C, 53.05; H, 5.52. Found: C, 52.98; H, 5.82. The fraction in tubes 31—61 presumably contains scandoside (III), but no detailed study of it has yet been undertaken because little sample is available.

The fraction in tubes 62—91 was treated in the same way as that in tubes 1—26 and 56.7 mg of powder were obtained. IR (KBr) cm^{-1} : 2700—2400, broad band about 1700, 1640. NMR (D_2O) τ : 2.30 (1H, d, $J=1$ cps, C-3), 3.92 (1H, m, C-7), 5.62 (2H, m, C-10), 6.87 (1H, t, C-5), 7.35 (1H, t, C-9). These signals correspond exactly to those of deacetylasperulosidic acid (IX). The following signals for scandoside (III) also appeared and integration indicated that there was about half as much III as substance (IX), τ : 2.50 (1H, C-3), 4.15 (C-7), 4.67 (C-1), 5.71 (C-10), 6.88 (C-9). PPC of scandoside (III): *Rf* (A) 0.08, (B) 0.05, (C) 0.27. PPC of deacetylasperulosidic acid (IX): *Rf* (A) 0.17, (B) 0.12, (C) 0.28.

The fraction in tubes 117—156 was treated in the same way and lyophilized to afford 102.8 mg of powder. Recrystallization from EtOH gave 10-acetylscandoside (X), mp 133—137° as fine needles. $[\alpha]_D^{25} -17.1^\circ$ ($c=1.02$, MeOH), UV λ_{max}^{EtOH} $m\mu$ (log ϵ): 235 (3.97). IR (KBr) cm^{-1} : 2700—2400, 1700, 1672, 1630. PPC: *Rf* (A) 0.26, (B) 0.15, (C) 0.44. *Anal.* Calcd. for $C_{18}H_{24}O_{12} \cdot H_2O$: C, 48.00; H, 5.82. Found: C, 47.71; H, 5.87. X (45 mg) was acetylated by the usual method with 1 ml each of pyridine and Ac_2O to yield 50 mg of colorless syrup. The NMR spectrum was found to be identical with that of an authentic specimen of VII. Substance (VII) (50 mg) was dissolved in ether and treated with excess CH_2N_2 -ether. The reaction product was recrystallized from ether to give 23 mg of VIII as fine needles, mp 133—135°. No depression of the mp was observed on mixing it with an authentic sample. $[\alpha]_D^{25} -87.1^\circ$ ($c=0.83$, MeOH), UV λ_{max}^{EtOH} $m\mu$ (log ϵ): 233 (3.99). The IR and NMR spectra were found to be identical with those of an authentic sample. *Anal.* Calcd. for $C_{29}H_{36}O_{17}$: C, 53.05; H, 5.52. Found: C, 52.76; H, 5.63.

The fraction in tubes 167—216 was also treated in the same way. Asperulosidic acid (XI) (78 mg) was obtained as a white powder, mp 127—131°. $[\alpha]_D^{25} +8.6^\circ$ ($c=0.98$, MeOH). UV λ_{max}^{EtOH} $m\mu$ (log ϵ): 234 (3.95). IR (KBr) cm^{-1} : 2700—2400, a broad absorption centered at 1700, 1630. NMR (D_2O) τ : 2.30 (1H, d, $J=1$ cps, C-3), 3.89 (1H, m, C-7), 6.89 (1H, t, C-9), 7.25 (1H, t, C-5). PPC: *Rf* (A) 0.29, (B) 0.14, (C) 0.44. *Anal.* Calcd. for $C_{18}H_{24}O_{12} \cdot 2H_2O$: C, 46.15; H, 6.03. Found: C, 46.52; H, 5.86.

Effect of Boiling a Methanolic Solution of Asperuloside (I)—I (1.5 g) was dissolved in 50 ml of MeOH and refluxed for 50 hr on a water bath. After filtration, the solvent was removed *in vacuo* to give an oily residue. This was dissolved in MeOH and passed through a charcoal column in the same solvent. The eluate was concentrated *in vacuo* giving 1 g of a colorless oil, which was subjected to counter-current distribution under conditions shown in Fig. 2. The fraction in tubes 65—85 was concentrated *in vacuo*. The resulting syrup was dissolved in MeOH. After treatment with charcoal, MeOH was removed *in vacuo*. The residue was dissolved in H_2O and lyophilized to give 85 mg of deacetylasperuloside (V) as a white powder, mp 117—118°. The IR, UV and NMR spectra were identical with those of an authentic specimen. The fraction in tubes 120—140 was concentrated *in vacuo*. The residue was recrystallized from H_2O -MeOH to recover 0.3 g of asperuloside (I). The residue from the fraction in tubes 175—200 was dissolved in MeOH, treated with charcoal and dried *in vacuo*. The residue was dissolved in H_2O and lyophilized to give 115 mg of daphylloside (XII) as a white powder, mp 99—101°. $[\alpha]_D^{25} +18.3^\circ$ ($c=0.93$, H_2O). UV λ_{max}^{MeOH} $m\mu$ (log ϵ): 236 (3.95). IR (KBr) cm^{-1} : 1730 (shoulder), 1710, 1635. NMR (D_2O) τ : 2.30 (1H, d, $J=1$ cps, C-3), 3.92 (1H, m, C-7), 4.98 (1H, d, C-1), 5.08 (2H, m, C-10) (The signals of the C-1 and C-10 protons overlapped the signal of HDO, so the spectrum in this region was not clear.), 6.25 (3H, s, $-COOCH_3$), 6.88 (1H, t, C-5), 7.27 (1H, t, C-9), 7.87 (3H, s, CH_3COO-). These spectra were all identical with those of an authentic specimen. PPC: *Rf* (A) 0.60, (B) 0.56, (C) 0.67. *Anal.* Calcd. for $C_{19}H_{26}O_{12} \cdot H_2O$: C, 49.14; H, 6.08. Found: C, 48.65; H, 5.73.

Effect of Boiling an Aqueous Solution of Paederoside (II)—A solution of 1 g of II in 30 ml of H_2O was heated for *ca.* 8 hr on a boiling water bath. After cooling, the resulting dark brown precipitate was filtered off and washed with a little H_2O . The filtrate and washing water were combined and concentrated *in vacuo* to give a slightly yellow syrup. This was dissolved in 10 ml of H_2O and subjected to the counter-

current distribution under the conditions shown in Fig. 3a. Paederoside(II) (655 mg) was recovered from the fraction in tubes 201—261. PPC of paederoside (II): *Rf* (A) 0.63, (B) 0.64, (C) 0.65.

The fraction in tubes 31—76 was concentrated *in vacuo* giving a syrup, which was dissolved in *ca.* 10 ml of H₂O and redistributed under the conditions given in Fig. 3b. The fraction in tubes 156—180 was concentrated *in vacuo*. A methanolic solution of the residue was treated by the conventional method with charcoal and concentrated *in vacuo*. The residue was dissolved in H₂O and lyophilized. 6-Epipaederosidic acid (XIII) (42 mg) was obtained as a white powder, mp 85—91°. $[\alpha]_D^{25} +26.4^\circ$ (*c*=0.58, MeOH). IR (KBr) cm⁻¹: 2700—2350, 1700, 1640. UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (log ϵ): 233 (3.91). NMR (D₂O) τ : 2.48 (1H, d, *J*=1 cps, C-3), 4.07 (1H, m, C-7), 4.68 (1H, d, *J*=5 cps, C-1), 5.00 (2H, m, C-10), 6.55 (3H, C-5, C-6'), 6.85 (1H, m, C-9), 7.67 (3H, s, CH₃COO-). PPC: *Rf* (A) 0.58, (B) 0.34, (C) 0.68. *Anal.* Calcd. for C₁₈H₂₄O₁₁S·2H₂O: C, 44.62; H, 5.83. Found: C, 44.42; H, 5.63.

The fraction in tubes 101—140 was also treated in the same way to furnish 35 mg of lyophilized powder. The NMR spectrum of the substance suggested that it was slightly impure 6-epipaederosidic acid (XIII). The fraction in tubes 180—201 was also treated in the same way to give 62 mg of lyophilized powder, mp 124—129°. $[\alpha]_D^{25} +54.4^\circ$ (*c*=0.68, MeOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (log ϵ): 234 (4.04). The IR and NMR spectra were found to be identical with those of an authentic sample of paederosidic acid (IV). PPC: *Rf* (A) 0.45, (B) 0.21, (C) 0.64. *Anal.* Calcd. for C₁₈H₂₄O₁₁S·2H₂O: C, 44.62; H, 5.83; S, 6.62. Found: C, 44.44; H, 5.71; S, 6.37.

Effect of Boiling a Methanolic Solution of Paederoside (II)—A solution of 1 g of II in 30 ml of MeOH was refluxed for 100 hr on a water bath and the reaction mixture was concentrated *in vacuo*. The residue was dissolved in 10 ml of the H₂O layer and fractionated by counter-current distribution. The fraction in tubes 101—140 was concentrated *in vacuo* and the resulting syrup was dissolved in MeOH, treated with charcoal, and the solvent was removed. The residue was dissolved in H₂O and lyophilized to give 18.8 mg of white powder. Little material was available so it was not examined further. However, it might well be deacetylasperuloside (V) judging from its IR spectrum. The fraction in tubes 216—271 was concentrated *in vacuo* yielding 553 mg of II. The fraction in tubes 276—300 was also concentrated *in vacuo* and treated with charcoal. The resulting aqueous solution was lyophilized to give 280 mg of paederosidic acid methyl ester (VI) as a white powder, mp 85—89°. $[\alpha]_D^{25} +16.8^\circ$ (*c*=1.20, MeOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (log ϵ): 236 (4.02). IR (KBr) cm⁻¹: 1700, 1635. NMR (D₂O) τ : 2.29 (1H, d, *J*=1 cps, C-3), 3.87 (1H, m, C-7), 4.94 (2H, m, C-10), 6.22 (3H, s, -COOCH₃), 6.54 (2H, m, C-6'), 6.89 (1H, t, C-5), 7.29 (1H, t, C-9), 7.62 (3H, s, CH₃CO-S-), PPC: *Rf* (A) 0.76, (B) 0.73, (C) 0.74. *Anal.* Calcd. for C₁₉H₂₆O₁₁S·2H₂O: C, 45.78; H, 6.07; S, 6.44. Found: C, 45.69; H, 5.57; S, 6.41.

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