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SESEBRINIC ACID, A CINNAMIC ACID DERIVATIVE FROM *SESELI SIBIRICUM*

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Key Word Index—*Seseli sibiricum*; Umbelliferae; coumarins; sesebrinic acid; synthesis.

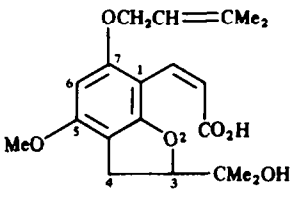
Abstract—A new cinnamic acid, sesebrinic acid, was isolated from the aerial parts of *Seseli sibiricum*; its structure was elucidated by chemical and spectral data and hemisynthesis. A number of its analogues were also synthesized.

INTRODUCTION

In continuation of our work on the chemical investigation of *Seseli sibiricum* Benth we have now investigated the aerial parts of this plant. Earlier, we reported the isolation of six new coumarins: sesebrin, sesebrinol, sibiricol, seselinal, sesibiricol and sibirinol from the roots and umbels of *S. sibiricum* [1, 2]. In this report we describe the isolation of a new cinnamic acid derivative (1) and the elucidation of its structure by chemical and spectral studies and by synthesis of it and some of its analogues.

RESULTS AND DISCUSSION

Repeated column chromatography of an *n*-hexane extract of the aerial parts of *S. sibiricum* led to the isolation of six coumarins: sesibiricin, osthol, coumurrayin, imperatorin, sesebrin and bergapten, previously reported from the roots and umbels, in addition to the new acid (1), named sesebrinic acid, $C_{20}H_{26}O_6$ ([M]$^+$ 362). Compound 1 dissolved slowly in aqueous sodium bicarbonate solution and has been characterized as 3-[3,4-dihydro-3-dimethylhydroxymethyl-5-methoxy-7-(3-methylbut-2-



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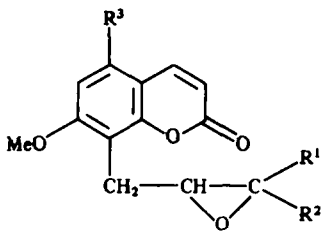
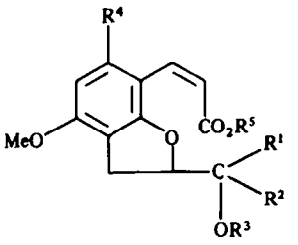
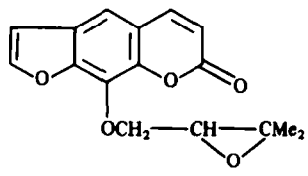


2 $R^1 = R^2 = Me$, $R^3 = OCH_2CH{=}CMe_2$
3 $R^1 = R^2 = R^3 = H$
4 $R^1 = R^2 = Me$, $R^3 = OMe$
5 $R^1 = R^2 = Me$, $R^3 = H$



7 $R^1 = R^2 = R^3 = R^4 = R^5 = H$
8 $R^1 = R^2 = Me$, $R^3 = R^5 = H$, $R^4 = OMe$
9 $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = H$
10 $R^1 = R^2 = R^4 = H$, $R^3 = Ac$, $R^5 = Me$
11 $R^1 = R^2 = R^5 = Me$, $R^3 = Ac$, $R^4 = H$



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enyloxy)benzofuran]-*cis*-2-propenoic acid on the basis of the following evidence. In the ^{1}H NMR spectrum (90 MHz) of **1**, two three-proton singlets at δ1.18 and 1.40 were assigned to $-CMe_2$ groups. The *gem*-dimethyl group of the prenyloxy chain showed up as two singlets at δ1.71 and 1.76. The olefinic proton at δ5.43 was a triplet (J = 7 Hz) whilst the methoxy protons resonated at δ3.80. The *O*-methylene and *O*-methine appeared as a multiplet centred at δ4.46. The benzylic methylene showed up as a double doublet at δ3.05 (J = 12, 7 Hz). The hydroxyl and carboxylic protons were hidden in a four-proton lump centred at δ6.00 which disappeared on deuteration leaving only a one-proton doublet at δ5.91 (J = 12 Hz) and a one-proton singlet at δ5.95 (H-6). The doublet at δ5.91 (J = 12 Hz) and the one at δ7.00 (J = 12 Hz) in the D_2O exchanged spectrum, each integrating for one proton, were attributable to the α,β-olefinic protons, respectively of α,β-unsaturated carboxylic acid chain. Sesebrin (**2**) on treatment with alkali followed by acidification yielded an acid which was found to be identical in all respects with natural sesebrinic acid (**1**). The transformation involves the opening of the lactone ring followed by an intramolecular reaction between the phenolate anion and the epoxide group forming the new ring [3–7]. The tendency of the intermediate phenolate anion to attack the epoxide ring is so pronounced that the treatment of sesebrin (**2**) with dimethyl sulphate in the presence of alkali does not give the expected product **15**. A number of 8-epoxyallyl and 8-epoxyallyloxy coumarins were subjected to the alkali followed by acid treatment when analogues of **1** were obtained. The coumarins used were 7-methoxy-8-epoxyallylcoumarin (**3**), sibiricin (**4**), meranzin (**5**) and heraclenin (**6**). The characterization of the reaction products (**7–9** and **12**) is based on spectral and chemical data.

Close inspection of ^{1}H NMR spectra of **1** and its analogues (**7–9** and **12**) revealed that the olefinic coupling constant in α,β-unsaturated carboxylic acid chains is around 12 Hz indicating *cis* orientation of the olefinic protons. An interesting observation was made in the course of the preparation of acetyl derivatives of the methyl esters of acids (**7–9**). The methyl ester of **7** on treatment with pyridine–acetic anhydride gave the corresponding acetate (**10**) but the methyl ester of **9** having a tertiary hydroxyl group, could not be acetylated by this method. However, treatment of the methyl ester of **9** with *p*-toluenesulphonic acid–acetic anhydride afforded the corresponding acetate (**11**), although, as the temperature of this acetylation was somewhat high, the α,β-unsaturated carboxylate side chain underwent isomerization giving exclusively the *trans* isomer (J = 16.2 Hz). Divakar and Rao [8] and Romesh and Srinivasan [9] observed that coumarin on treatment with methyl sulphate in the presence of alkali formed *o*-methoxy *cis*-cinnamic acid which is contrary to the observation of Sehgal *et al.* [10] that similar conditions produced a *trans* predominated isomeric mixture. The former conforms to our observation.

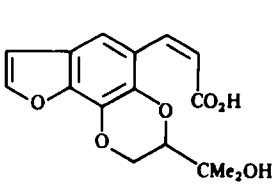
To substantiate further the formation of *cis*-cinnamic acid, the alkylative ring opening of coumarin was carried out using ethyl sulphate and allyl bromide in the presence of alkali when only *o*-ethoxy- and *o*-allyloxy-*cis*-cinnamic acids, **13** and **14** respectively, were obtained.

Sesebrinic acid (**1**) is not an artefact as its isolation did not involve the use of a base at any stage and the acid was observed in the crude extract using TLC. It is probable that the physiological conditions in the plant caused the formation of the intermediate phenolate anion which became rearranged to give **1**.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded at 90 MHz in $CDCl_3$ unless otherwise stated. The plant material was collected from Kashmir (voucher specimen no. 1725 deposited at the Plant Survey Division of R.R.L., Jammu). The identity of the known products was established by comparison of their physical data with those of their authentic samples. These include mps, UV fluorescence, R_f values, ^{1}H NMR and MS.

Isolation. Dried and powdered aerial parts of *S. sibiricum* (4 kg) were extracted with *n*-hexane, concd to give an oily residue (200 g) and chromatographed on neutral Al_2O_3 (3.3 kg) (deactivated with 10% H_2O). Fractions (275, 750 ml each) were collected as the eluting solvent was progressively changed to increasing polar mixtures of *n*-hexane, *n*-hexane–C_6H_6, C_6H_6–$CHCl_3$ and $CHCl_3$. Fractions 1–180 were combined and rechromatographed over silica gel. The *n*-hexane eluate gave an oil having no UV fluorescence. Elution with *n*-hexane–C_6H_6 yielded successively sesibiricin, mp 121–122°, osthol, mp 83–84° and coumurrayin, mp 155–156°. Fractions 181–216 on concn yielded a residue which was chromatographed over silica gel. Elution with C_6H_6 gave successively imperatorin, mp 102°, sesebrin, mp 111–112° and bergapten, mp 188–190°. Fractions 222–266, eluted with C_6H_6, were combined and rechromatographed over neutral Al_2O_3. Fractions eluted with C_6H_6–$CHCl_3$ mixture were dried *in vacuo* to yield a residue which on crystallization from Me_2CO–*n*-hexane afforded **1** as needles (171 mg), mp 155–156°, R_f 0.68 [silica gel, $CHCl_3$: MeOH (4:1)]; IR ν_{max}^{KBr} cm^{-1}: 3375 (OH), 1700



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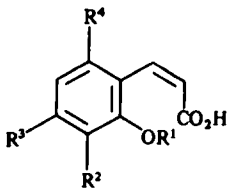

13 R^1 = Et, R^2 = R^3 = R^4 = H

14 R^1 = $CH_2CH{=}CH_2$, R^2 = R^3 = R^4 = H

15 R^1 = Me, R^2 = $CH_2{-}CH(O){-}CMe_2$, R^3 = OMe

R^4 = $OCH_2CH{=}CMe_2$

(CO), 1627 (double bond in conjugation with CO), 1605, 1495, 1462, 1380, 1125. MS: *m/z* 362 $[M]^+$, 294 $[M-CH_2CH=CMe_2+H]^+$, 250 $[294-CO_2]$, 236 $[250-CH_2]$, 218 $[236-H_2O]$, 190 $[218-CO]$.

Hemisynthesis of sesebrinic acid (1). An aq. soln of NaOH (5%, 5 ml) was added gradually to a stirred soln of sesebrin (2) in MeOH (5 ml) during 30 min. After concn the residue was washed with Et_2O to remove unreacted 2, acidified with HCl and left overnight in the cold. The solid was filtered and crystallized from Me_2CO–*n*-hexane to give fine needles (140 mg), identical with the natural sesebrinic acid (1) on comparison of ^1H NMR, MS, TLC and mmp.

7-Methoxy-8-epoxyallylcoumarin (3). Umbelliferone (2 g) in dry Me_2CO (60 ml) was refluxed with allyl bromide (5 ml) in the presence of dry K_2CO_3 (8 g) for 2 hr. After the usual work up the product was crystallized from Me_2CO–*n*-hexane to yield 7-allyloxycoumarin (1.7 g), mp 80°. A soln of 7-allyloxycoumarin (1.5 g) in *N,N*-dimethylaniline (8 ml) was refluxed for 8 hr. The mixture was cooled and poured into crushed ice containing HCl. The precipitated solid was collected and crystallized from aq. MeOH to give 7-hydroxy-8-allylcoumarin (0.7 g), mp 162–163°, ^1H NMR (Me_2CO-d_6): δ3.57 (2H, *d*, *J* = 6 Hz, benzylic protons), 4.95 (1H, *d*, *J* = 10 Hz, –C(H)=C(H)H), 5.03 (1H, *d*, *J* = 17 Hz, –C(H)=C(H)H), 6.00 (1H, *m*, –CH=CH_2), 6.15 (1H, *d*, *J* = 9.5 Hz, H-3), 6.88 (1H, *d*, *J* = 8 Hz, H-6), 7.38 (1H, *d*, *J* = 8 Hz, H-5), 7.64 (1H, *d*, *J* = 9.5 Hz, H-4), 9.74 (1H, *br s*, OH, D_2O exchangeable). A soln of 7-hydroxy-8-allylcoumarin (0.6 g) in dry Me_2CO (20 ml) was refluxed with MeI (2 ml) in the presence of dry K_2CO_3 (2 g) for 6 hr. After the usual work up the residue was crystallized from $CHCl_3$ when 7-methoxy-8-allylcoumarin was obtained as needles (0.5 g), mp 141–142°, ^1H NMR: δ3.62 (2H, *d*, *J* = 6.5 Hz, benzylic protons), 3.92 (3H, *s*, OMe), 4.98 (1H, *d*, *J* = 10 Hz, –C(H)=C(H)H), 5.06 (1H, *d*, *J* = 17 Hz, –C(H)=C(H)H), 5.93 (1H, *m*, –CH=CH_2), 6.22 (1H, *d*, *J* = 9.5 Hz, H-3), 6.83 (1H, *d*, *J* = 8 Hz, H-6), 7.33 (1H, *d*, *J* = 8 Hz, H-5), 7.62 (1H, *d*, *J* = 9.5 Hz, H-4). A soln of 7-methoxy-8-allylcoumarin (400 mg) in $CHCl_3$ (10 ml) was treated with a soln of perbenzoic acid (300 mg) in $CHCl_3$ (5 ml) and left at room temp. After 2 hr the soln was washed with aq. $NaHCO_3$ and H_2O, dried (Na_2SO_4) and evapd to dryness *in vacuo*. The residue on crystallization from EtOAc–*n*-hexane afforded 3 (330 mg) as needles, mp 158–159°, ^1H NMR: δ2.63 (2H, *m*, benzylic protons), 2.82–3.38 (3H, *m*, –CH_2–CH(O)–CH_2), 3.95 (3H, *s*, OMe), 6.22 (1H, *d*, *J* = 9.5 Hz, H-3), 6.81 (1H, *d*, *J* = 8 Hz, H-6), 7.32 (1H, *d*, *J* = 8 Hz, H-5), 7.58 (1H, *d*, *J* = 9.5 Hz, H-4).

3-(3,4-Dihydro-3-hydroxymethyl-5-methoxybenzofuran)-cis-2-propenoic acid (7). 3 (200 mg) was treated with aq. NaOH followed by HCl and on working up (as in the hemisynthesis of 1 described above) 7 was obtained as needles (from Et_2O), mp 135–137°, ^1H NMR: δ3.06 (1H, *d*, *J* = 7.5 Hz, one of the benzylic protons), 3.14 (1H, *d*, *J* = 9.5 Hz, one of the benzylic protons), 3.72 (2H, *m*, –CH_2OH), 3.84 (3H, *s*, OMe), 4.96 (1H, *m*, –CH_2–CH(O)–), 5.94 (1H, *d*, *J* = 12 Hz, –CH=CHCO$_2$H), 6.08 (2H, *m*, OH and CO_2H, D_2O exchangeable), 6.42 (1H, *d*, *J* = 8 Hz, H-6), 6.93 (1H, *d*, *J* = 12 Hz, –CH=CHCO$_2$H), 7.23 (1H, *d*, *J* = 8 Hz, H-7); MS: *m/z* 250 (M^+), 233, 232, 219, 206, 203, 201. The methyl ester of 7 (Prepared using Et_2O–CH_2N_2), a pale yellow gum, ^1H NMR (CCl_4): δ2.86 (1H, *br s*, OH, D_2O exchangeable), 3.04 (2H, *d*, *J* = 7 Hz, benzylic protons), 3.58 (2H, *m*, –CH_2OH), 3.72 (3H, *s*, CO_2Me), 3.81 (3H, *s*, OMe), 4.81 (1H, *m*, –CH_2–CH(O)–), 5.74 (1H, *d*, *J* = 12 Hz, –CH=CHCO$_2$H), 6.30 (1H, *d*, *J* = 8 Hz, H-6), 6.81 (1H, *d*, *J* = 12 Hz, –CH=CHCO$_2$H), 7.44 (1H, *d*, *J* = 8 Hz, H-7).

Methyl 3-(3,4-dihydro-3-hydroxymethyl-5-methoxybenzofuran)-cis-2-propenoate acetate (10). The methyl ester of 7 (100 mg) on treatment with Ac_2O–pyridine gave the acetate (10) as a gum. ^1H NMR (CCl_4): δ2.03 (3H, *s*, OCOMe), 2.88 (1H, *dd*, *J* = 7.5, 16 Hz, one of the benzylic protons); 3.12 (1H, *dd*, *J* = 7.5, 16 Hz, one of the benzylic protons), 3.64 (3H, *s*, CO_2Me), 3.80 (3H, *s*, OMe), 4.16 (2H, *d*, *J* = 7 Hz, –CH_2OAc), 4.92 (1H, *m*, –CH_2–CH(O)–), 5.70 (1H, *d*, *J* = 12 Hz, –CH=CH–CO_2Me), 6.33 (1H, *d*, *J* = 8 Hz, H-6), 6.92 (1H, *d*, *J* = 12 Hz, –CH=CHCO$_2$Me), 8.01 (1H, *d*, *J* = 8 Hz, H-7).

3-(3,4-Dihydro-3-dimethylhydroxymethyl-5-methoxybenzofuran)-cis-2-propenoic acid (9). 5 (100 mg) in MeOH (10 ml) on treatment with aq. NaOH (5%, 5 ml) at room temp. followed by HCl and work up gave 9 (75 mg), needles from aq. MeOH, mp 185–187°, ^1H NMR (Me_2CO-d_6): δ1.05, 1.15 (3H each, *s*, 2 Mes), 2.96 (2H, *d*, *J* = 8.5 Hz, benzylic protons), 3.73 (5H, *s*, on D_2O exchange 3H, *s*, OMe, OH, CO_2H), 4.53 (1H, *t*, *J* = 8.5 Hz –CH_2–CH(–CMe$_2$OH)), 5.74 (1H, *d*, *J* = 13 Hz, –CH=CH–CO_2H), 6.31 (1H, *d*, *J* = 8.5 Hz, H-6), 6.97 (1H, *d*, *J* = 13 Hz, –CH=CHCO$_2$H), 7.76 (1H, *d*, *J* = 8.5 Hz, H-7); MS: *m/z* 278 $[M]^+$, 234, 220, 219, 191. The methyl ester of 9 (prepared by using Et_2O–CH_2N_2), a pale yellow gum, ^1H NMR (CCl_4): δ1.06, 1.17 (3H each, *s*, 2 Mes), 2.51 (1H, *br s*, OH, D_2O exchangeable), 2.95 (1H, *d*, *J* = 9.5 Hz, one of the benzylic protons), 3.0 (1H, *d*, *J* = 7.5 Hz, one of the benzylic protons), 3.62 (3H, *s*, CO_2Me), 3.75 (3H, *s*, OMe), 4.42 (1H, *dd*, *J* = 9.5, 7.5 Hz, –CH_2–CH(–CMe$_2$OH)), 5.67 (1H, *d*, *J* = 12.6 Hz, –CH=CHCO$_2$Me), 6.21 (1H, *d*, *J* = 8 Hz, H-6), 6.78 (1H, *d*, *J* = 12.6 Hz, –CH=CHCO$_2$Me), 7.40 (1H, *d*, *J* = 8 Hz, H-7).

Methyl 3-(3,4-dihydro-3-dimethylhydroxymethyl-5-methoxy-benzofuran)-trans-2-propenoate acetate (11). The methyl ester of 9 (50 mg) was heated with Ac_2O (1 ml) in the presence of *p*-toluenesulphonic acid (5 mg) at 80° for 1 hr. The mixture was allowed to cool, poured in H_2O and the product extracted into Et_2O and the extract washed with aq. $NaHCO_3$, H_2O and dried (Na_2SO_4). Evapn of Et_2O yielded 11 as a pale yellow gum, ^1H NMR (CCl_4): δ1.45, 1.57 (3H each, *s*, 2 Mes), 1.96 (3H, *s*, OCOMe), 3.02 (2H, *d*, *J* = 8.5 Hz, benzylic protons), 3.70 (3H, *s*, CO_2Me), 3.81 (3H, *s*, OMe), 5.10 (1H, *t*, *J* = 8.5 Hz, –CH_2–CH(–CMe$_2$OAc), 6.31 (1H, *d*, *J* = 8 Hz, H-6), 6.41 (1H, *d*, *J* = 16.2 Hz –CH=CHCO$_2$Me), 7.09 (1H, *d*, *J* = 8 Hz, H-7), 7.44 (1H, *d*, *J* = 16.2 Hz, –CH=CHCO$_2$Me).

3-(3,4-Dihydro-3-dimethylhydroxymethyl-5,7-dimethoxybenzofuran)-cis-2-propenoic acid (8). A soln of 4 (150 mg) in MeOH (10 ml) on treatment with aq. NaOH (5%, 5 ml) at room temp. followed by acidification gave 8 (120 mg), needles from aq. MeOH, mp 153–155°, ^1H NMR: δ1.17, 1.37 (3H each, *s*, 2 Mes), 3.11 (1H, *d*, *J* = 10 Hz, one of the benzylic

protons), 3.15 (1H, *d*, $J = 6.5$ Hz, one of the benzylic protons), 3.78, 3.82 (3H each, *s*, 2 OMes), 4.43–4.87 (3H, *m*, on D_2O exchange 1H, *s*, –O–CH, OH and CO_2H), 5.90 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 6.02 (1H, *s*, H-6), 6.97 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H); MS: *m/z* 308 $[M]^+$, 275 $[M - H_2O - Me]^+$, 250 $[M - MeCOCH_3]^+$, 206 $[250 - CO_2]$, 205, 203, 173.

Effect of NaOH *on heraclenin: formation of* **12**. A soln of **6** (1 g) was treated with aq. NaOH (20 ml) at room temp. On acidification of the soln and working up as above, the acid (**12**) was obtained as needles (from MeOH) (830 mg), mp 162–164°, ^{1}H NMR: δ1.38, 1.40 (3H each, *s*, 2 Mes), 4.07 (2H, *dd*, $J = 8$, 14 Hz, –OCH$_2$–CH–), 4.46 (1H, *dd*, $J = 8$, 8 Hz, –OCH$_2$–CH–O–), 6.06 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 6.18 (2H, *br s*, OH and CO_2H, D_2O exchangeable), 6.64 (1H, *d*, $J = 2$ Hz, furan β-proton), 7.17 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 7.28 (1H, *s*, aromatic proton), 7.58 (1H, *d*, $J = 2$ Hz, furan α-proton); MS: *m/z* 304 $[M]^+$, 246 $[M - MeCOCH_3]$, 202 $[246 - CO_2]$, 200, 147, 145. Methyl ester of **12** (prepared by using Et_2O–CH_2N_2), pale yellow gum (100 mg), ^{1}H NMR: δ1.36, 1.40 (3H each, *s*, 2 Mes), 2.54 (1H, *s*, OH, D_2O exchangeable), 3.67 (3H, *s*, CO_2Me), 4.05 (2H, *dd*, $J = 8$, 14 Hz, –OCH$_2$–CH–O–), 4.44 (1H, *dd*, $J = 8$, 8 Hz, –OCH$_2$–CH–O–), 6.00 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 6.67 (1H, *d*, $J = 2$ Hz, furan β-proton), 7.11 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 7.37 (1H, *s*, aromatic proton), 7.54 (1H, *d*, $J = 2$ Hz, furan α-proton).

o-*Ethoxy*-cis-*cinnamic acid* (**13**). Prepared according to the lit. [9], mp 103–104°, ^{1}H NMR (Me_2CO-d_6): δ1.40 (3H, *t*, $J = 7$ Hz, –OCH$_2$CH$_3$), 4.07 (2H, *q*, $J = 7$ Hz, –OCH$_2$Me), 5.84 (1H, *d*, $J = 12.5$ Hz, –CH=CHCO$_2$H), 6.72–7.68 (5H, *m*, 4 aromatic protons and –CH=CHCO$_2$H), 8.22 (1H, *br s*, CO_2H, D_2O exchangeable).

o-*Allyloxy*-cis-*cinnamic acid* (**14**). Prepared according to the lit. [9], mp 67–68°, ^{1}H NMR (CCl_4): δ4.52 (2H, *d*, $J = 5$ Hz, –OCH$_2$–), 5.33 (2H, *dd*, $J = 10$, 17 Hz, =CH$_2$), 5.73–6.33 (1H, *m*, –OCH$_2$CH=CH$_2$), 5.91 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 6.68–7.62 (4H, *m*, aromatic protons), 7.72 (1H, *d*, $J = 12$ Hz, –CH=CHCO$_2$H), 10.72 (1H, *s*, CO_2H, D_2O exchangeable).

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