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A NEW AROMATIC NITROSULFONE FROM *CARDIOSPERMUM CORINDUM*

D. ADINARAYANA,*

Department of Chemistry, S.V. University Post-Graduate Centre, Kurnool 518001, India

K. NARAYANA RAO,

Department of Botany, S.V. University, Tirupati 517502, India

and M. SARADA

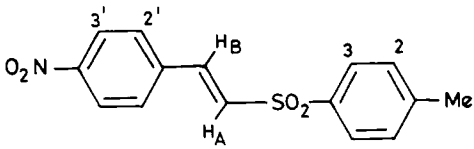
Department of Chemistry, S.P.W. College, Tirupati 517502, India

ABSTRACT.—Dried leaves of *Cardiospermum corindum* yielded two, novel-type aromatic nitrosulfones [**1**,**2**]. The structures were established by spectroscopic analyses and synthesis. Compounds **1** and **2** were assigned the structures, 1-methyl-4- { [2-(4-nitrophenyl) ethenyl } sulfonyl benzene and 1- { [2-methoxy-2-(4-nitrophenyl) ethyl] sulfonyl } 4-methyl benzene, respectively.

Morphologically, the climber *Cardiospermum corindum* L. (Sapindaceae) reflects spectacular adaptive diversities of development of yellow-tinged petals with supra basal scales presumably designed to favor cross pollination. The inflated fruit and worm-like seed with cordate hylum are advantageous for seed dispersal (1,2). Recently, this plant has attracted the attention of phytochemists (3-7). The present study is an attempt to discover new chemical compounds to match the relatively advanced morphology of the genus.

Dried leaves of *C. corindum* collected near Tirupati, Chittoor District, Andhra Pradesh, India, were successively extracted with petrol, C_6H_6, and Me_2CO. Five subsequent MeOH extracts each deposited a solid on cooling, which resulted in the isolation (see Experimental) of 3′,4′-di-*O*-methylluteolin-7-β-D-glucuronide (8), an orange compound [**1**], and, finally, a light yellow, crystalline product [**2**].

The orange compound, according to eims, possessed the composition $C_{15}H_{13}NO_4S$. The compound had no optical activity. The ir spectrum displayed strong bands at 1340 and 1510 cm^{-1}, as well as at 1140 and 1320 cm^{-1}, indicative of the presence of $-NO_2$ and $-SO_2$ groupings, respectively. The ^{1}H-nmr and ^{13}C-nmr spectra suggested that the compound **1** was 1-methyl-4- { [2-(4 nitrophenyl) ethenyl] sulfonyl } benzene. This formulation was supported by the base peak fragment at *m/z* 139 ($Me.C_6H_4.SO^+$) in the ms. On electron impact, *p*-tolyl vinyl sulfones are known to undergo predominantly vinyl migration to oxygen with subsequent cleavage of the sulfur oxygen bond (9).



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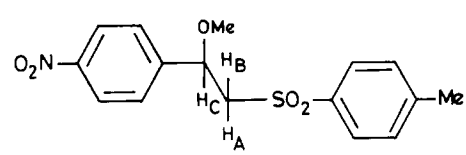

2

Structure **1** was corraborated upon comparison with a synthetic sample, prepared from 4-nitrobenzaldehyde and [(4-methyl-phenyl) sulfonyl] acetic acid as per the modified Baliah method of synthesis of vinylic sulfones (10,11).

The light yellow isolate **2** contained the elements of MeOH, additional to those of

1, according to eims. ^{1}H nmr and ^{13}C nmr revealed an unchanged aromatic pattern, disappearance of the vinylic system and addition of MeO groupings, all features suggestive of structure **2**. The base peak in the ms was represented by a fragment with *m/z* 166, attributable to the benzylic ion, $O_2NO_6H_4CH(OMe)^+$, and helping to define the location of the MeO groupings. An authentic specimen of the previously unknown 1-{ [2-methoxy-2-(4-nitrophenyl) ethyl] sulfonyl } -4-methyl benzene was produced by methoxide catalyzed addition of MeOH to **1**.

The two aromatic nitro compounds **1** and **2** represent a novel type of natural product. It is rare to find in plants sulfones with an aromatic nitro group. However, the presence of nitro containing compounds is not new to plant chemistry (12-14).

The sulfoxides and sulfones are considered to be the enzymatic oxidation products of simple sulfur compounds. Several general biosynthetic pathways have been elucidated leading to the formation of complex chemical compounds in highly organized systems as well as through several complex enzymes (15). It may be assumed that the sulfur-containing amino acids are precursors for the formation of sulfones in plants, but the nature and number of enzymatic steps remain to be established.

The biochemical elaboration of the unusual compounds **1** and **2** is in good correlation with the advanced floral elaboration of *C. corinudum* (1,2), as compared to the other, morphologically less-specialized, species of Sapindaceae.

EXPERIMENTAL

GENERAL.—Nmr spectra were recorded on Brucker WH-90 and HX-270 instruments and eims on a VG Micromass 7070 F instrument, IP70 eV, ion source, 220°. Mps were determined in capillary tubes uncorrected (ct) or on the microscope (m).

PLANT MATERIAL.—Leaves of *C. corindum* were collected and air dried. A herbarium voucher specimen has been deposited at the Department of Botany of the Sri Venkateswara University, Tirupati, Andhra Pradesh, India.

EXTRACTION OF **1**.—The material (1.5 kg) was successively extracted with hot petrol (60-80°) (10 liters), C_6H_6 (10 liters), Me_2CO (10 liters), and x 5 with MeOH total of (10 liters). On cooling, each of the MeOH extracts deposited a ppt, sequentially numbered S-1 to S-5. S-2 was rich in 3′,4′-di-*O*-methylluteolin glucuronide identified upon comparison with an authentic specimen (8), whereas S-3 contained additional quantities of the glucuronide admixed with another product [**1**] forming large orange needles. Mechanical separation of these, followed by recrystallization from EtOAc-pyridine (9:1) gave a crop of orange-yellow needles (30 mg), mp 182-183° (m).

Precise mass determination of the product [**1**] (M^+ 303.0561) revealed its composition as $C_{15}H_{13}NO_4S$ (M^+ 303.0565). Recording of the cd curve, within the range 230-400 nm, proved the compound to be devoid of optical activity. Ir, ^{1}H-, and ^{13}C-nmr spectra were recorded and, together with the eims, suggested the structure **1**.

SYNTHESIS OF **1**.—For confirmation, authentic **1** was synthesized essentially following literature procedures (10,11). [(4-Methylphenyl) sulfonyl] acetic acid (1.1 g), 4-nitrobenzaldehyde (0.75 g), and benzylamine (125 ml) were dissolved in HOAC (3.5 ml) and refluxed for 100 min. The crystalline reaction product was washed with MeOH and recrystallized from EtOAc-MeOH (1:1) (40 ml) to give pale yellow needles (0.82 g, 55.1%), mp 182-183° (m) [lit. 182-183° (16)]; ir ν max (KBr) 1620 (t-CH=CH), 1510, 1340 (NO_2), 1310-20 (double band), 1140 (SO_2) 950 (t-OH=CH); ^{1}H nmr ($CDCl_3$) δ 2.44 (3H, *s*, Me), 6.96 (*d*, J=15 H_z 1H, ethylenic proton 1), 7.30 (*d*, J=9 H_z, 2H, H-2 6), 7.57, (*d*, J=9 H_z, 2H, H-2′,6′), 7.63 (*d*, J=15 H_z, 1H ethylenic proton 2), 7.78 (*d*, J=9 H_z 2H, H-3, 5), 8.15 (*d*, J=9 H_z, 2H, H-3′,5′); ^{13}C nmr ($CDCl_3$) δ 21.7 (CH_3), 124.3, 128.0, 129.0, 130.2, 132.1, 136.9, 138.7, 145.1 (all arom); eims *m/z* (rel. int) 303 (M^+, 10), 239 (M^+-SO_2,4), 192 (3), 178 (3), 148 (4), 139 (Me-$C_6H_4SO^+$, 100), 131 (3), 102 (7), 91 (19), 65 (10). All spectral data were identical with those of the natural product.

ISOLATION OF **2**.—From S-4, an additional quantity of 3′,4′-di*O*-methylluteolin-7-glucuronide was obtained. The final extract yielded a deposit (S-5), that could be separated into a part soluble in MeOH. On keeping the MeOH portion aside for a day, pale yellow crystals (40 mg) were deposited mp 97-99° (ct) for which all the spectroscopic data were recorded and interpreted as being in accord with the structure **2**.

SYNTHESIS OF **2**.—An authentic specimen of racemic **2** was prepared. A solution of **1** (606 mg) in MeOH (100 ml) containing MeOHa (20 mg) was refluxed for 10 h and then evaporated to an oil; this was taken up in $CHCl_3$, the solution was washed with 0.01 M HCl and H_2O, dried and concentrated to dryness to give a rapidly crystallizing oil (628 mg, 94.1%). Recrystallization from MeOH (3 ml) gave a product still containing minute amounts of **1**. Tlc on Si gel ($CHCl_3$-hexane, 2:1, 5 developments), elution of the major band with $CHCl_3$, and recrystallization from MeOH, afforded an analytical specimen of **2** as virtually colorless needles mp 105° (m) (Found: C, 57.26, H, 5.05, N, 4.10; S, 9.53. $C_{16}H_{17}NO_5S$ requires C, 57.30, H, 5.11, N, 4.18, s, 9.56); ir ν max (KBr) cm^{-1} 1510, 1340 (NO_2), 1300 (three bands), 1140 (SO_2); ^1H nmr ($CDCl_3$) δ 2.45 (3H, *s* aromatic Me), 3.16 (3H, *s*, OMe), 3.22-3.29 (1H, *dd*, H_A (or H_B), 3.56-3.64 (1H, *dd*, H_B or (H_A), 4.87 (1H, *dd*, H_C), 7.34 (2H, *d*,*J*=9 H_z, H-3), 7.46 (2H, *d*,*J*=9 H_z, H-2′), 7.79 (2H, *d*,*J*=9 H_z, H-2), and 8.20 (2H, *d*,*J*=9 H_z, H-3′), ^{13}C-nmr ($CDCl_3$) δ (assignment) 21.4 (arom. Me), 57.0 (OMe), 63.1 (CH_2), 77.1 (benzyl-C), 124.0, 127.3, 127.9, 129.6, 137.4, 138.5, 144.7, 146.2 (all arom. C); eims *m/z* (rel. int) 335 (M^+, 2), 180 (35), 179 (33), 166 [$O_2NC_6H_4CH(OMe)$: 100], 150 (10), 142 (9), 120 (9), 91 (23). All spectral data were in agreement with those of the isolated pale yellow product.

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