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β,β-DIMETHACRYLOPHENONES AND A CHROMANONE FROM *NAMA HISPIDUM* AND *N. JOHNSTONII*

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Key Word Index—*Nama hispidum*; *N. johnstonii*; Hydrophyllaceae; leaf resin; dimethacrylophenones; chromanone.

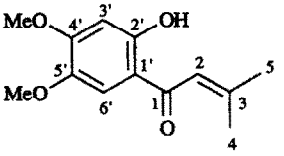
Abstract—A β,β-dimethacrylophenone and the corresponding chromanone were isolated from the leaf resin of *Nama hispidum*. The leaf exudate of *N. johnstonii* contains another β,β-dimethacrylophenone as colouring matter.

INTRODUCTION

The genus *Nama* L. comprises some 40–50 species, occurring from the southwestern United States to South America, primarily in dry habitats. It is the second largest genus in the Hydrophyllaceae, comprising small annuals as well as woody subshrubs [1, 2]. In the course of continuing studies on exudate flavonoids, *N. johnstonii* attracted our interest when we noticed that the newspaper in which it was pressed was stained intensely yellow. When we later obtained samples *of N. hispidum* A. Gray var. *hispidum*, this was also analysed. Although an earlier report on two different species of *Nama* lists several flavonoid aglycones [2], no such product was found in the species we analysed. Instead, we identified two dimethylacrylophenones and a chromanone as colouring matter in their leaf resins.

RESULTS AND DISCUSSION

The major pigment present in the leaf resin of *N. hispidum* is compound **1**, which formed fine yellow needles, mp 84–84.5°, after recrystallization from hexane. On polyamide TLC it appeared as a dark brown spot (UV_{366}) at R_f 0.91 which turned fluorescent red on spraying with NA. The mass spectrum of **1** ($[M]^+ = m/z$ 236.10486) provided the molecular formula $C_{13}H_{16}O_4$. Examination of the ^1H NMR spectrum of **1** revealed two aromatic protons as singlets, two aromatic methoxyl groups (singlets), a strongly hydrogen-bonded OH signal at low field (singlet) and a pair of vinyl methyl resonances each exhibiting long range coupling to a single vinyl proton. The ^{13}C spectrum of **1** displayed resonances for two aromatic methoxyls, two aliphatic methyls, a carbonyl, two aromatic CHs, one vinyl CH and three aromatic C-Os. The remaining two signals were assigned to a disubstituted olefinic carbon and an aromatic carbon attached to neither C nor O. The foregoing data are in complete accord with the β,β-dimethacrylophenone structure proposed for **1**.



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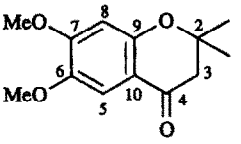

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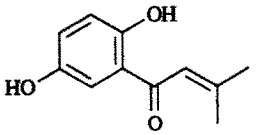

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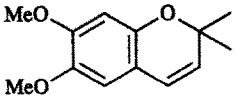

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Compound **2** was obtained from the same plant in small amounts as a gum which crystallized on standing. When viewed under UV_{366}, TLC spots of **2** showed a strong blue fluorescence (R_f) 0.58 on polyamide (solvent as above). The molecular ion and other prominent ions in the mass spectrum of **2** were the same as for **1** although the relative intensities were different. The ^1H NMR spectra of **1** and **2** showed some similarities and several notable differences. The aliphatic methyl groups in **2** gave rise to one upfield singlet instead of two vinyl doublets, and the one proton vinyl multiplet (δ6.63) in the spectrum of **1** appeared upfield as a two proton aliphatic methylene singlet (δ2.67) in that of **2**. The H-bonded OH signal seen in the spectrum of **1** at low field (δ13.26) was absent from the spectrum of **2**. The most obvious difference between the ^{13}C NMR spectra of **1** and **2** was the replacement of the side chain olefinic signals (CH and C) of **1** by upfield signals in **2** corresponding to CH_2 and C–O carbons. These data support the chromanone structure for **2**.

In order to relate the two substances, a sample of **1** was warmed in ethanol with a trace of hydrochloric acid, affording a sample which was identical to **2** (R_f, UV, NMR). Although both **1** and **2** have been previously synthesized [3, 4] during studies undertaken to prove the structure of ageratochromene (**4**), neither has been previously reported as a natural product.

Compound **3** was isolated as a dark yellow solid whose spots on TLC plates reacted rapidly when sprayed with a dilute solution of Tollen's reagent (ammoniacal silver) indicating aromatic hydroxyl groups *ortho* or *para* to one another. On polyamide TLC, the product appeared under UV_{366} as a dull yellow brown spot (R_f 0.47), which turned dark reddish-violet on spraying with NA. The mass spectrum of **3** showed a molecular ion at *m/z* 192 and suggested the molecular formula $C_{11}H_{12}O_3$. The ^1H and ^{13}C NMR spectra revealed the presence of a *β,β*-dimethacryloyl group in **3** just as in **1**. The presence of a H-bonded OH signal indicated that a OH-2′ was also present in **3** as in **1**. In addition, the proton spectrum revealed a typical 1,2,4-trisubstituted benzene ring pattern. The downfield shifts of the benzene CH resonances in the carbon spectrum showed that none was located between two C-Os, requiring the location of the second OH *para* to the one at C-2′, in accord with the positive Tollen's spray result mentioned above. The ^{13}C NMR resonances of the benzene ring portion of **3** are in good agreement with those reported for 2-acetylhydroquinone [5], and the structure of **3** is thus shown to be *β,β*-dimethacryloylhydroquinone.

To the best of our knowledge, **1–3** are new natural products. The possibility that **2** is an artefact arising from ring closure of **1** during storage of the plant material or from isolation procedures cannot be overlooked. If **2** is in fact a genuine natural product, it joins the very limited number of naturally occurring chromanones thus far reported. The only phytochemical study on *Nama* species of which we are aware [2] reports the presence of six flavonoid aglycones in a dichloromethane–ethyl acetate extract of ground aerial parts of *N. lobbii* and *N. rothrockii*. It is assumed that these flavonoids are constituents of an exudate, as are the phenolics reported here.

EXPERIMENTAL

Nama johnstonii was collected in October 1984 in Mexico, Edo. Coahuila, on Hwy 30, about 11 miles northeast of Puerto de Ventanillas and 47 miles northeast of San Pedro de Las Colonias at an elevation of 2670 feet (T. R. & R. K. Van Devender 84-589, R. P. Neilson; voucher at ARIZ). *Nama hispidum* var. *hispidum* was collected in September 1985 in the U.S., in Sandoval Co., New Mexico, on Hwy 44, some 4 miles northeast of Zia Pueblo (G. Yatskievych 85-308, M. D. Windham; voucher at IND). Whereas we had only one herbarium specimen of *N. johnstonii*, 44 g of air-dried material of *N. hispidum* var. *hispidum* were available. On rinsing with Me_2CO, the latter yielded some 280 mg of leaf resin which was chromatographed on a small column of silica, eluted with toluene and increasing portions of methylethyl ketone and MeOH. Compound **1** was eluted with 2% methylethyl ketone, whereas **2** was eluted later, after addition of MeOH. Compound **1** was further purified by prep. centrifugal TLC on silica (see below). Compound **2** was purified by passage over Sephadex LH-20, followed by prep. TLC on silica. In the case of *N. johnstonii*, most of the exudate material was extracted from the newspaper used in the plant press. On polyamide TLC [toluene–petrol (100–140°)–MeCOEt–MeOH 12:6:2:1], this material exhibited one major spot. The relevant product was isolated by prep. TLC on silica (toluene–methylethyl ketone 9:1) and further purified by passage through a pipette filled with Sephadex LH-20 (eluted with MeOH) to yield **3**.

1-(2-*hydroxy*-4,5-*dimethoxyphenyl*)-3-*Methyl*-2-*buten*-1-*one* (**1**). The sample (70 mg) was further purified in two batches by centrifugal circular TLC (Chromatotron) on a 1-mm-thick silica layer employing hexane–Et_2O (4:1) as eluent. The major product (42 mg) was recrystallized from hexane affording fine yellow needles (33 mg) mp 84–84.5° (lit. [3] mp 86.5°); UV λ_{max}^{MeOH} nm: 360, 292, 262; (lit. [3] λ_{max} nm: 361, 290, 262); EIMS, *m/z* (rel. int.): 236 $[M]^+$ (22), 221 $[M-Me]^+$ (100), 205 (5), 181 (26), 165 (8), 137 (5), 78 (6), ^1H NMR ($CDCl_3$): *δ* 13.26 (*s*, OH-2′), 7.12 (*s*, H-6′), 6.63 (*m*, H-2), 6.47 (*s*, H-3′), 3.91 (*s*, OMe), 3.87 (*s*, OMe), 2.20 (*d*, *J* = 2 Hz, 3 × H-5), 2.04 (*d*, *J* = 2 Hz, 3 × H-4); ^{13}C NMR: 194.5 (C-1), 161.0 (C-3), 156.2 (C-2′ + C-4′), 141.5 (C-5′), 120.1 (C-2), 112.4 (C-1′), 111.2 (C-6′), 100.7 (C-3′), 56.7 (OMe), 56.1 (OMe), 28.1 (C-5), 21.3 (C-4). [A spectrum run in Me_2CO-d_6 produced discreet signals for C-2′ and C-4′ (*δ* 157.2, 157.3)].

2,2-*Dimethyl*-6,7-*dimethoxy*-4-*chromanone* (**2**). UV λ_{max}^{MeOH} nm: 342, 276, 240 (lit. [3] λ_{max} nm: 342, 275, 238); EIMS, *m/z* (rel. int.): 236 $[M]^+$ (70), 221 $[M-Me]^+$ (100), 205 (4), 165 (20), 137 (12), 69 (13), 58 (11), 43 (34); ^1H NMR ($CDCl_3$), *δ* 7.27 (*s*, H-5), 6.40 (*s*, H-8), 3.91 (*s*, OMe), 3.88 (*s*, OMe), 2.67 (*s*, H-3), 1.46 (*s*, 2 × Me); ^{13}C NMR: 191.1 (C-4), 156.3[a] (C-7), 156.3[a] (C-9), 144.0 (C-6), 112.3 (C-10), 106.3 (C-5), 100.5 (C-8), 79.6 (C-2), 56.2 (OMe), 56.2 (OMe), 48.4 (C-3), 26.6 (2 × 2-Me). [a]Assignments may be interchanged.

Conversion of **1** *to* **2**. A sample of **1** (9 mg) in EtOH (2 ml) containing 1 drop of conc HCl was refluxed for several hr then evapd to dryness. Purification by centrifugal circular TLC on a 1 mm silica layer eluted with hexane–$CHCl_3$ (1:1) afforded a gum (5 mg) which crystallized on standing. Examination of this material by TLC, UV and ^1H NMR showed it to be identical to **2**.

1-(2,5-*dihydroxyphenyl*)-3-*Methyl*-2-*buten*-1-*one* (**3**). UV λ_{max}^{MeOH} nm: 380, 272; EIMS, *m/z* (rel. int.): 192 $[M]^+$ (15), 177 $[M-Me]^+$ (100), 137 (26), 83 (9), 55 (14); ^1H NMR (DMSO-d_6): *δ* 11.76 (*s*, OH-2′), 9.16 (*br s*, OH-5′), 7.24 (*d*, *J* = 2.8 Hz, H-6′), 6.98 (*dd*, *J* = 2.8, 9 Hz, H-4′), 6.90 (*m*, H-2), 6.79 (*d*, *J* = 9 Hz, H-3′), 2.14 (*d*, *J* = 1.2 Hz, 3 × H-5), 2.02 (*d*, *J* = 1.2 Hz, 3 × H-4); ^{13}C NMR: 195.1 (C-1), 157.9 (C-3), 154.5 (C-2′), 149.3 (C-5′), 124.0 (C-4′), 121.1 (C-1′), 120.7 (C-2), 118.4 (C-6′), 114.6 (C-3′), 27.7 (C-5), 21.2 (C-4).

Accurate mass measurement of the molecular ion in the MS of **1** and low resolution EIMS of **1** and **2** were determined on a VG Micromass 7070 mass spectrometer at 70 eV. NMR: 200 MHz (^1H) and 50 MHz (^{13}C).

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