

Hewlett-Packard oscillator (range 0–20 KHz) and a Hewlett-Packard Type 130 oscilloscope as the zero indicator.

The conductivity cell consisted of a sintered alumina tube with 3 mm inner diameter. The electrodes were rings made of 0.8 mm Ø Pt wire spaced 30 mm apart. The current leads were 0.2 mm Ø Pt wire. Prior to each run the cell constant was determined by means of 0.1 N KCl solution, and values around 20 cm⁻¹ were found. The compound salt was filled into a silica glass crucible and melted, whereupon the conductivity cell was lowered into place. The salts were kept melted in an atmosphere of purified argon for several hours, and then slowly cooled in the inert atmosphere. Measurements were performed both at increasing and decreasing temperature, and at each temperature by the following frequencies: 1, 2, 4, 8, and 12 HKz.

The error in the resistance measurements vary from 0.05 % in the low conductivity region to approximately 1 % in the region with high conductivity. Additional error, however, are introduced through the procedure for extrapolation to infinite frequency. This is estimated to some ± 5 % as an average.

The temperature was measured by means of a calibrated Pt/Pt10Rh thermocouple placed outside the crucible at equal distances from the two electrodes in the middle of the temperature-gradient free zone. The accuracy in the temperature measurements is better than ± 1°C.

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Chemical Constituents of the Genus *Dahlia*

II. The Isolation of two Aromatic Compounds: Naringenin Trimethylether and Fraxidin

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During the past years we have investigated the light petroleum and ether extractives from species belonging to the genus *Dahlia* (Compositae) with special regard to the content of polyacetylenic compounds. Several times we have isolated non-acetylenic constituents from the lipophilic extracts. We now wish to report about two of these compounds.

One was isolated in an amount of 25 mg from the leaves and stems (182 g of fresh plant material) of *Dahlia lehmanni* Hieron. It was a colourless compound melting at 123.5–124.5° with an ultraviolet spectrum exhibiting maxima at 282 and 229 mμ (ϵ : 19 000 and 31 500). The infrared spectrum displayed a strong carbonyl band at 1670 cm⁻¹ besides bands at 3050, 1610, 1575, and 1510 cm⁻¹ (aromatic-type bands), 1250 and 1108 cm⁻¹ (—C—O—bands). The infrared spectrum excluded OH. The Shinoda test^{1a} was positive (pink). The data support the assumption that the compound could be a flavanone. The ultraviolet spectrum is in close accordance^{1b} with that of naringenin (5,7,4'-trihydroxy-flavanone). Microanalytical data for the isolated compound agree with the formula for the trimethylether of naringenin, *i.e.* C₁₈H₁₈O₅ (Found: C 68.43; H 5.77. Calc. for C₁₈H₁₈O₅: C 68.78; H 5.77). Apparently this compound has never been isolated from any

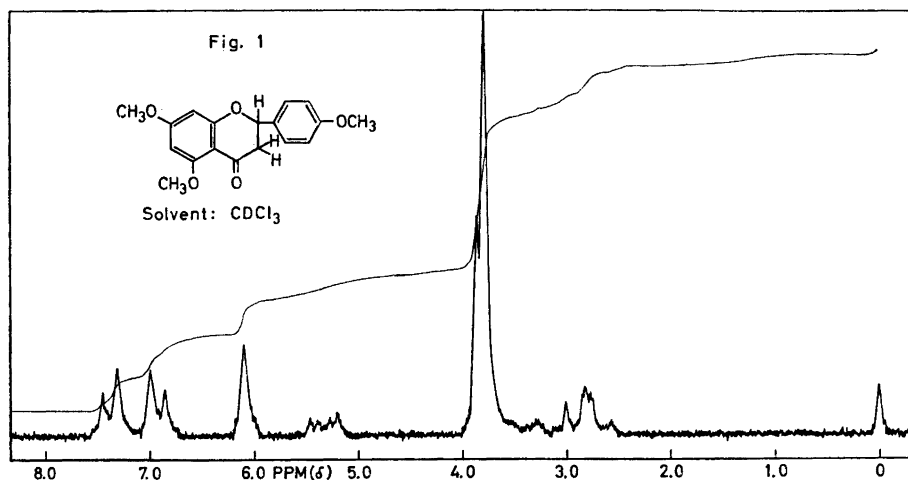


Fig. 1.

natural source but is known as a synthetic product.²⁻⁴ The literature mentions different melting points for naringenin trimethyl-ether: 117.2°–117.8°,² 123°,³ and 124°⁴ of which two are in good agreement with our value. The supposed structure, *i.e.* 5,7,4'-trimethoxy-flavone, is consistent with the NMR-spectrum (Fig. 1) of the compound. The signals from the methyl protons appear at δ 3.8 ppm with an intensity of 9 protons. H-6 and H-8 give

a single un-split signal (2 protons) at δ 6.1 ppm. H-2', H-6', and H-3', H-5' appear as two doublets at δ 6.9 ppm and δ 7.4 ppm. The coupling constant is 8.5 cps. The protons of the γ -pyrone ring constitute an ABX system whose AB part (H_A-3, H_B-3) appears at δ 2.9 ppm as a multiplet. The X part (H-2) appears as a double doublet at lower field, (δ 5.3 ppm). Finally, we have synthesised the flavanone by cyclization of 2'-hydroxy-4',6',4-tri-

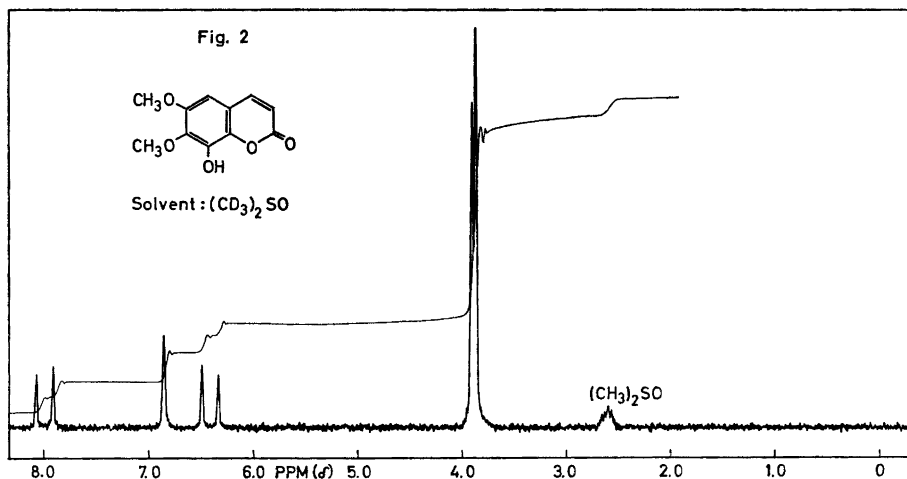


Fig. 2.

methoxy-chalcone according to the procedure given by Geissman and Clinton,⁵ and the natural product proved to be identical with the synthetic specimen in every respect.

A second compound was isolated from the tubers of *Dahlia barkeriae* Knowles & Westc. During evaporation of the ether extracts, a nearly colourless compound precipitated. 900 g of fresh tubers gave 125 mg of the compound. The crystals were removed and recrystallized from chloroform-light petroleum, giving a compound melting at 192–194°. In solution the compound exhibited blue fluorescence. The infrared spectrum was indicative of OH and aromaticity. Further, the infrared spectrum displayed a strong carbonyl band at 1675–1680 cm⁻¹. The ultraviolet spectrum (in ethanol) had the following peaks: 223, 257, and 311 m μ (ϵ : 17 000, 4200, and 9600). With sodium hydroxide, the 257 and the 311 m μ bands are shifted to 276 and 330 m μ , respectively. These data suggested that the natural product was a coumarin. The NMR-spectrum (Fig. 2) shows two one proton doublets at δ 6.4 ppm ($J = 9$ cps) and δ 8.0 ppm ($J = 9$ cps), corresponding to the α resp. the β proton in the lactone ring. Two signals with nearly the same chemical shifts at δ 3.9 ppm are assigned to two O-substituted methyl groups in an aromatic ring. A signal from a single phenolic proton (not shown on the figure) appears at δ 9.3 ppm, and, finally, there is a signal at δ 6.85 ppm corresponding to a single non-coupling aromatic proton. Thus the compound should be a hydroxy-dimethoxy-coumarin, *i.e.* C₁₁H₁₀O₅. The microanalytical results fit this formula rather well

(Found: C 59.81; H 4.77. Calc. for C₁₁H₁₀O₅: C 59.50; H 4.54). Among many possible isomers, fraxidin (8-hydroxy-6,7-dimethoxy-coumarin), isolated⁶ from *Fraxinus excelsior* L. (Oleaceae) seems to be identical with the compound from *Dahlia barkeriae*. Fraxidin^{6,7} is reported to melt at 196–197°, and in the ultraviolet region it has the following peaks:⁸ 223, 256, and 311 m μ (ϵ : 19 900, 5000, and 10 000). By means of dimethyl sulphate, the compound was methylated in potassium carbonate solution and transformed into the methyl derivative with melting point 104°, agreeing with that reported^{6,7} for 6,7,8-trimethoxy-coumarin (m.p. 104°). Thus it seems reasonable to conclude that the compound isolated from *Dahlia barkeriae* is fraxidin.

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