

1. Seyferth, D., Burlitch, J. M., Dertouzos, H. and Simmons, Jr., H. D. *J. Organomet. Chem.* **7** (1967) 405.
2. Kagan, H. B., Basselier, J.-J. and Luche, J.-L. *Tetrahedron Letters* **1964** 941.
3. Barrow, K. D. and Spotswood, T. M. *Tetrahedron Letters* **1965** 3325.
4. McMillan, I. and Stoodley, R. J. *Tetrahedron Letters* **1966** 1205.
5. Audier, H. E., Fétizon, M., Kagan, H. B. and Luche, J. L. *Bull. Soc. Chim. France* **1967** 2297.
6. Imbach, J.-L., Doomes, E., Cromwell, N. H., Baumgarten, H. E. and Parker, R. G. *J. Org. Chem.* **32** (1967) 3123.
7. Seyferth, D., Mui, J. Y.-P. and Burlitch, J. M. *J. Am. Chem. Soc.* **89** (1967) 4953.
8. Bevan, W. J., Haszeldine, R. N. and Young, J. C. *Chem. Ind. (London)* **1961** 789.

Received June 19, 1968.

Some Unusual Flavonoids from *Myrica gale* L.

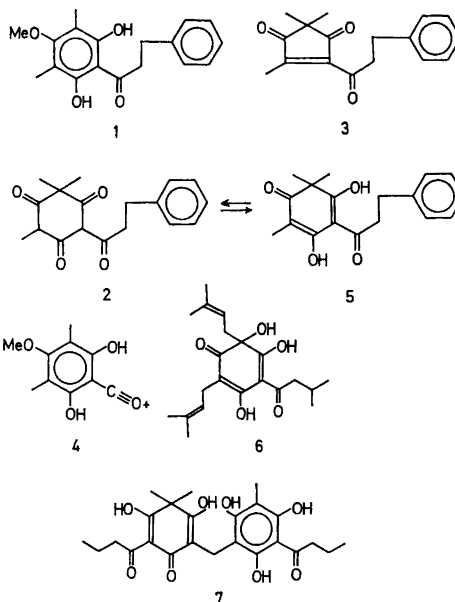
THORLEIF ANTHONSEN, INGER
FALKENBERG, MORTEN LAAKE,
ANNA MIDELFART and THORVALD
MORTENSEN

Organic Chemistry Laboratories, Norwegian
Institute of Technology, University of Trond-
heim, Trondheim, Norway

A small bush with a strong aromatic scent, *Myrica gale* L. (bog myrtle) which is very common on moist ground and on peat land in this country, has for ages been utilized as a moth repellent and as a hop substitute in the brewing of beer. A number of terpenoids and flavonoids are known to be present in the plant.¹

We now wish to report the isolation of three new aromatic compounds *1*, *2*, and *3* from an acetone extract of fruits from this bush. *1* was isolated by column and thin-layer chromatography as yellow needles and recrystallized from ether-petroleum

ether (m.p. 116–117°C) [λ_{\max} (EtOH) 224 (14 200), 280 (17 400), and 350 (4200) nm; IR: 3600, 1620, 1500, and 1455 cm^{-1}]. The molecular composition of this compound was established as $\text{C}_{18}\text{H}_{20}\text{O}_4$ by accurate measurement of the molecular ion peak (calc. 300.1362, found 300.1365). The NMR spectrum shows two aromatic methyl groups (7.92, 6H *s*) and one methoxy methyl group (6.32, 3H *s*). An A_2B_2 system (τ_{A} 6.60, τ_{B} 7.00) and a five proton singlet at 2.80 suggest that the compound might be a dihydrochalcon. Finally a two proton singlet at 0.45 due to two identical hydrogen-bonded hydroxy protons is in good agreement with the constitution *1*.



Additional evidence can be found in the mass spectrum where the base peak at m/e 195 ($\text{C}_{10}\text{H}_{11}\text{O}_4^+$) is due to a favoured cleavage leading to the oxonium ion *4*. The relative positions of the methoxy and methyl groups were assigned on the basis of symmetry considerations.

2 was isolated from a more polar fraction from the column and proved to be an isomer of *1* (calc. for $\text{C}_{18}\text{H}_{20}\text{O}_4$ 300.1362, found 300.1365) (m.p. 138–139°C) [λ_{\max} (EtOH) 350 (19 900) nm].

The NMR spectrum in deuteriochloroform solution shows that *2* is a mixture of

several tautomers, not unexpected since it contains four enolizable keto groups. However, in deuteriomethanol solution only one olefinic (8.14, 3H *s*) and two aliphatic (8.67, 6H *s*) methyl groups are seen. The five proton singlet at 2.77 and the A₂B₂ system at 6.75 and 7.08 indicate the presence of the phenylpropionyl group.

Thus a tautomer like **5** satisfies the spectral data.

The mass spectrum of **2** shows a small peak at *m/e* 195. The molecular ion furnishes the base peak, and there are important peaks at *m/e* 168 (C₈H₁₂O₃⁺, 39 %) and *m/e* 230 (C₁₄H₁₄O₃⁺, 30 %) due to losses of neutral fragments as benzylketene and dimethylketene, respectively.

Finally we have isolated by preparative GLC an oily compound (**3**) which contains a five membered ring [λ_{\max} (EtOH) 243 (10 000) and 305 (620) nm; IR: 1750, 1705, 1605, 1500, and 1455 cm⁻¹] (calc. for C₁₇H₁₈O₃, 270.1255, found 270.1257) and which might have been formed *in vivo* by extrusion of formaldehyde from **2**.

The NMR spectrum contains peaks due to the phenylpropionyl group (2.83, 5H *s*, 6.82 and 7.05 A₂B₂) one olefinic (7.90, 3H *s*) and two identical aliphatic methyl groups (8.88, 6H *s*). In the mass spectrum the base peak at *m/e* 91 can be formulated as the tropylium ion C₇H₇⁺. High abundance peaks are also found at *m/e* 270 (M⁺,

62 %), *m/e* 242 (C₁₆H₁₆O₃⁺, 54 %), *m/e* 199 (C₁₃H₁₁O₃⁺, 32 %), and *m/e* 138 (C₈H₁₀O₂⁺, 53 %) due to losses of carbon monoxide (242) a further extrusion of an isopropyl radical (199) and the direct loss of benzylketene (138) from the molecular ion peak.

The similarity in the chemical constitution of the components of hop (*Humulus lupulus*), e.g. humulone (**6**)² and bog myrtle (*Myrica gale*) and their alternative use in brewing should be noted. Moreover, it may also be pointed out that there is a relationship between these compounds and the *Dryopteris* acylphloroglucinols such as flavaspadic acid (**7**).³ Thus **2** is 3-(β -phenylpropionyl)-5-methyl filicinic acid.

Further work on the chemical constituents of *Myrica gale* L. is in progress.

All NMR spectra were run on a Varian A60A instrument and the mass spectra on AEI MS 902 with a PDP8 computer.

1. Hegnauer, R. *Chemotaxonomie der Pflanzen*, Birkhäuser, Basel 1969, Band V, p. 141.
2. De Keukeleire, D. and Verzele, M. *Tetrahedron* **26** (1970) 385.
3. Penttilä, A. and Sundman, J. *J. Pharm. Pharmacol.* **22** (1970) 393.

Received June 11, 1971.

KEMISK BIBLIOTEK
Den kgl. Veterinær- og Landbohøjskole