Separation of Phenolic Alkaloids

The alkaloid mixture (1 g) was separated on silica TLC plates with $CHCl_3$–MeOH (1:1, v/v). The alkaloid bands were detected by using the side strip spraying technique with the reagent platinum iodide as the detecting reagent. The separated bands were scraped off and continuously extracted with methanol to recover the alkaloidal material.

N-Methylhomotyramine

The major band yielded 108 mg of light brown crystals. These were purified on a short alumina column eluted with EtOAc. This produced white crystals (14·1 mg), m.p. 105–108°, ν_{max}3400, 1610 cm^{-1}, λ_{max}205, 222 and 277 nm (ϵ 5, 030, 7, 019 and 1, 856). M^+ = 165·1162. Calculated for $C_{10}H_{15}NO_3$:165·1154. (Found: C, 72·48; H, 9·18; N, 8·73; O, 9·80. $C_{10}H_{15}NO$ requires C, 72·69; H, 9·15; N, 8·48; O, 9·68%.)

N-Methyltyramine

The second largest band from the TLC separation gave crystals from $CHCl_3$ m.p. 127–129°. (Literature, m.p. 130°.)[5] The u.v., λ_{max} 205, 227, 277 (ϵ 5, 192, 7, 550, 1, 416). M^+ = 151·1003. Calculated for $C_9H_{13}NO_3$. 151·0997.

Separation of Non-phenolic Alkaloids

$CHCl_3$ (10 ml) was added to the non-phenolic fraction (0·5 g) and a waxy solid separated out and was filtered off. The $CHCl_3$ was removed, and acetone (25 ml) added to the brown gum. A white crystalline material remaining undissolved had m.p. 198–200° and was optically inactive, λ_{max}209 nm (ϵ 7, 770), ν_{max}3401, 1661, and 1616 cm^{-1}. The mass spectrum showed (M^+) = 333·204. Calculated for $C_{18}H_{27}N_3O_3$:333·205. The base peak appeared at *m/e* 213, and other major peaks at *m/e* 316, 302, 259, 188 and 104. (Found: C, 63·84; H, 8·16; O, 14·40; N, 12·60. $C_{18}H_{27}N_3O_3$ requires C, 63·92; H, 8·09; O, 14·66; N, 12·91%). The acetone soluble brown gum was further purified on an alumina column packed in EtOAc. The first four fractions which were eluted with EtOAc–$CHCl_3$ (3:1, v/v) showed a single spot on TLC in several systems and were combined. The oil so obtained was distilled at 163° under reduced pressure and the product analysed. (Found: C, 70·55; H, 8·82; N, 2·44; O, 18·67. $C_{35}H_{51}NO_7$ requires C, 70·32; H, 8·6; N, 2·34; O, 18·74%).

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LABIATAE

ISOLATION AND IDENTIFICATION OF ALKANES FROM THREE TAXA OF *MONARDA*

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Abstract—Nine *n*-alkanes were isolated and identified from the herb of *Monarda punctata* var. *maritima*, seven from *Monarda punctata* var. *fruticulosa*, and five from *Monarda fistulosa* var. *mollis*. These alkanes ranged from $C_{27}H_{56}$ to $C_{35}H_{72}$. In all three taxa, the odd numbered alkanes were generally present in larger amount than the even numbered ones.

PHYTOCHEMICAL studies of the genus *Monarda* have been limited primarily to the essential oils,[1–4] aldehydes[4] and flavanoids.[2,5–9] Various species of *Monarda* are of importance today in landscaping, gardening and beekeeping[10,11] and are still employed for food,[12–14] flavoring[15,16] and medicinal[17,18] purposes.

This paper presents the results of a continuation of a biosystematic survey of the genus *Monarda* by the authors in a search for additional chemical constituents. The taxa analyzed were *M. fistulosa* L. var. *mollis*, Bentham *M. punctata* L. var. *fruticulosa* (Epling) Scora and *M. punctata* L. var. *maritima* Cory.

RESULTS AND DISCUSSION

In all three taxa studied even and uneven numbered *n*-alkanes were found ranging from $C_{27}H_{56}$ to $C_{35}H_{72}$; the uneven numbered alkanes were generally present in larger amounts by weight than the even numbered ones. The $C_{33}H_{68}$ was the largest component in all three taxa tested.

The genus *Monarda* is subdivided into the subgenera *Monarda* and *Cheilyctis*. *Monarda fistulosa* var. *mollis* belongs to the former, which is tetraploid and also the most evolved of the two subgenera on the basis of anatomical, cytological, morphological, and other criteria.[12] Despite its biological advancement, the least number of alkanes were found in this taxon, namely, those ranging from C_{31} to C_{35} only. *Monarda punctata* var. *fruticulosa* and *M. punctata* var. *maritima* belong to the diploid subgenus *Cheilyctis*, which is considered the more basic one. Variety *fruticulosa* yielded six alkanes, namely, C_{29} to C_{35} with C_{28} present in trace amounts only. Variety *maritima*, however, which is regarded as the most advanced of the *punctata* complex, yielded more alkanes, namely, those from C_{27} to C_{35}.

EXPERIMENTAL

All plants were grown at the University of California, Riverside, from rootstocks collected by the senior author in Michigan and Texas. Leaves and stems were harvested for analysis just before flowering. All voucher specimens are deposited in the herbarium of the Department of Life Sciences, University of California, Riverside.

[1] R. W. SCORA, *Am. J. Botany* **54**, 446 (1967).
[2] C. H. BRIESKORN and G. MEISTER, *Arch. Pharm.* **298**, 435 (1935).
[3] J. W. BRANDEL and E. KREMERS, *Chem. Centralblatt* **2**, 1007 (1901).
[4] W. KARRER, *Konstitution und Vorkommen der Organischen Pflanzenstoffe*, p. 1207, Birkhauser Verlag, Basel (1958).
[5] H. WAGNER, H. HORHAMMER, G. AURNHAMMER and L. FARKAS, *Tetrahedron Letters* 1837 (1967).
[6] L. HORHAMMER, G. AURNHAMMER and H. WAGNER, *Phytochem.* **9**, 899 (1970).
[7] J. B. HARBORNE, *Phytochem.* **3**, 151 (1964).
[8] S. ASEN, *Proc. Am. Soc. Hort. Sci.* **78**, 586 (1961).
[9] P. KARRER and R. WIDMER, *Helv. Chiml Acta* **10**, 67 (1927).
[10] L. H. BAILEY, *The Standard Cyclopedia of Horticulture*, MacMillan, London (1917).
[11] D. HENSON, *Proc. Oklahoma Acad. Sci.* **19**, 57 (1941).
[12] W. W. ROBBINS, J. P. HARRINGTON and B. FREIRE-MARRECO, *Bur. Amer. Ethnol. Bull.* **55**, 1 (1916).
[13] E. L. STURTEVANT, *New York State Dept. Agr.* 27 *Ann. Rept*, 1918, Vol. 2 (2) 1.686 (1919).
[14] J. W. FEWKES, *Am. Anthropol* **9**, 14 (1896).
[15] E. F. CASTETTER, Uncultivated native plants used as sources of Food N. Mex. *Univ. Bull.* **226**, 34 (Ethnobiol. Studies in Am. South W. No. 1 (1935)).
[16] W. C. MUENCHER, *Garden Spice and Wild Plants*. Comstock Publ. Assoc. Ithaca, New York (1955).
[17] R. H. CLARK, *Proc. Trans. R. Soc. Canada* **20**, 469 (1926).
[18] Dispensatory of the 20th ed. Philadelphia, London Lippincot Co. (1918).

Isolation of the Alkanes

Coarsely milled leaves of *M. punctata* var. *maritima* (540 g) were extracted continuously with 7·5 l. petroleum (30–60°) and evaporated to dryness to yield 13·71 g residue. This residue was recrystallized several times from acetone to give 1·21 g of white plates. An i.r. spectrum of the isolate was indicative of alkanes. There was no absorption in the u.v. spectrum. A mass spectrum showed a typical alkane fragmentation pattern with the highest mass ion at *m/e* 492. The alkanes from variety *M. punctata* var. *fruticulosa* and *M. fistulosa* var. *mollis* were isolated in a similar manner. The yields are tabulated in Table 1.

TABLE 1. ALKANE YIELDS FROM THREE SPECIES OF *Monarda*

	Percent Composition of Alkanes		
Alkanes	*M. punctata* var. *maritima*	*M. punctata* var. *fruticulosa*	*M fistulosa* var. L. *mollis*
$C_{27}H_{56}$	3·75	—	—
$C_{28}H_{58}$	2·22	trace	—
$C_{29}H_{60}$	6·20	6·96	—
$C_{30}H_{62}$	3·59	4·13	—
$C_{31}H_{64}$	16·04	17·92	5.46
$C_{32}H_{66}$	9·83	10·81	2·70
$C_{33}H_{68}$	32·52	37·30	55·59
$C_{34}H_{70}$	12·72	14·75	9·31
$C_{35}H_{72}$	13·07	8·09	26·91

Dry weight of plant, 540·0 g 185·0 g and 168·0 g for *M. punctata* var. *maritima*, *M. punctata* var. *fruticulosa* and *M. fistulosa* var. *mollis* respectively. Yield of alkanes 1·21 g, 0·11 g and 0·15 g respectively.

Gas Chromatographic Identification of Alkanes

Analysis of the isolate was effected by gas chromatography after the method of Tin Wa *et al.*,[19] using a Varian 1520 G.C. with thermodetector, a Varian 475 digital integrator for area computation and a Beckman recorder. The column used was 183 cm long, 0·64 cm o.d., stainless steel, packed with 10% UC W-98 coated on 80–100 mesh Gas Chrom. Q. The injector and detector temperatures were 300°, the column temperature 280° isothermal. Helium was the carrier gas. The isolates separated under these conditions into 9 distinct peaks in one taxon, and 7 and 5 peaks in the two other taxa. These peaks were identified through comparison with reference samples as *n*-heptacosane $C_{27}H_{56}$, *n*-octacosane $C_{28}H_{58}$, *n*-nonacosane $C_{29}H_{60}$, *n*-triacontane $C_{30}H_{62}$, *n*-hentriacontane $C_{30}H_{62}$, *n*-dotriacontane $C_{32}H_{66}$, *n*-tritriacontane $C_{33}H_{68}$, *n*-tetratriacontane $C_{34}H_{70}$ and *n*-pentatriacontane $C_{35}H_{72}$.

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[19] W. TIN, N. R. FARNSWORTH and H. H. S. FONG, *Lloydia* **32**, 509 (1969).