

*Carapanaubine*⁴ Éluée par un mélange benzène-CHCl₃; cristallisée dans l'éther C₂₃H₂₈O₆N₂ (M⁺ 428), F 218–219°, [α]_D = –115°, identifiée avec un échantillon de référence

*Rauvoxinine*⁴ Éluée par le CHCl₃, C₂₃H₂₈O₆N₂ (M⁺ 428), F 199°, [α]_D = +64°, identifiée avec un échantillon de référence

Diméthoxy-10,11 isomitraphylline (I) Éluée par le CHCl₃, (M⁺ 428), F 142°, [α]_D +15° UV nm (log ε) 218 (4,44), 280 (3,71), épaulements à 245 et 300 IR ν cm⁻¹ (KBr) 1710 (double bande) et 1620 système oxindolique RMN (CDCl₃, δ ppm) 1,13 (d 3 H, J = 6,5 Hz) méthyle 18, 3,58 (s, 3H) ester méthylique, 3,85 et 3,86 (2s de 3H) méthoxyles aromatiques, 4,35 (octet, 1H, J₁ = 6,5 Hz et J₂ = 2,5 Hz) hydrogène en 19, 6,52 et 6,92 (s, 1H) protons aromatiques respectivement en 12 et en 9, 7,38 (d, 1H, J = 1 Hz) H en 17, 8,7 (singulet élargi disparaissant par deutériation, 1H) NH indolique

Ces données sont compatibles avec la structure I la position du signal de résonance du méthyle 18 dans le spectre de RMN de I jointe à la valeur de la constante de couplage J_{H19-H20} = 2,5 Hz indiquent une jonction *trans* des cycles D/E 15α,20β et une configuration α pour le méthyle 18, ces données permettent ainsi de placer ce nouvel alcaloïde dans le groupe V de la classification des oxindoles publiée par l'un de nous⁵ (J-L P)

Le déblindage important du proton aromatique en 9 (6,92 ppm) et l'apparition d'un signal centré à 0,8 ppm, attribuable à l'un des protons portés par le carbone 14, situé dans le champ du cycle benzénique, permet de classer cet alcaloïde dans le groupe V_A⁵ où la liaison C₂–C₇ est 'anti' par rapport au doublet de l'azote Nb

*Isomérisation de I→II (diméthoxy-10,11 mitraphylline)*⁵ 130 mg de I sont dissous à l'ébullition dans une solution aqueuse d'acide acétique à 5% et chauffés pendant 4 hr Après alcalinisation du milieu par l'ammoniaque et extraction par du CH₂Cl₂ on obtient 120 mg d'un produit, cristallisé dans l'éther (90 mg) C₂₃H₂₈O₆N₂ (M⁺ 428) F 181°, [α]_D –28° UV nm (log ε) 218 (4,44), 280 (3,70), IR (KBr) ν cm⁻¹ 1710 et 1610, RMN (CDCl₃) par rapport au spectre de I⁺ plus de proton en C₁₄ vers 0,8 ppm, protons H₁₂ et H₉ respectivement à 6,62 et 6,76 δ

⁴ M HESSE, *Indolalkaloïde in Tabellen*, p 134 et supplément 1968, p 143, Springer-Verlag, Berlin (1964)

⁵ J-L POUSSET, J POISSON, R J SHINE et M SHAMMA, *Bull Soc Chim. Fr.* 2766 (1967)

Key Word Index—*Cabucala madagascarensis*, Apocynaceae, oxindole alkaloids, 10,11-dimethoxy isomitraphylline

ASCLEPIADACEAE

IDENTIFICATION OF THE ALKANES IN SIX *ASCLEPIAS* SPECIES*

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INVESTIGATIONS of *Asclepias* have dealt mainly with the cardiac and pregnane glycosides¹ present, although some attention has been directed toward the alkaloids^{2,3} and terpenes⁴⁻⁶. In this paper we wish to present our analysis of the *n*-alkanes for six species.

TABLE 1 *Asclepias* TOTAL ALKANE CONTENT (%)^{*}

	C ₂₃	C ₂₄	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	C ₃₂	C ₃₃	Alkenes [†]
<i>A. amplexicaulis</i>	<1	<1	5.5	4.8	59.6	3.6	18.2	<1	8.3	<1	<1	—
<i>A. incarnata</i>	4.7	1.7	3.7	1.9	16.2	7.8	55.9	2.8	5.3	<1	<1	—
<i>A. lanuginosa</i> [‡]			4.6	2.1	12.3	3.8	19.1	6.0	36.3	5.2	10.6	+
<i>A. syriaca</i>	2.9	3.2	3.7	2.0	14.5	2.6	32.9	8.1	25.6	2.1	3.1	+
<i>A. verticillata</i>	<1	<1	<1	<1	1.7	1.4	22.3	7.8	63.6	1.6	1.6	+
<i>A. viridiflora</i> [‡]			2.0	<1	4.3	1.9	15.5	3.6	63.1	3.6	6.0	+

^{*} Based on the alkane content only

[†] Based on the difference in G C peaks before and after Br₂ treatment

[‡] Formerly classed under the *Acerates* genus

Although there does not appear to be any definite chemotaxonomic correlations to be drawn, several interesting points can be observed from our results listed in Table 1. For instance, four of the species have one alkane present as about 60% of the total alkane fraction. The remaining two have several equally prominent constituents; of these two, *A. lanuginosa* contains a higher proportion of the higher alkanes than *A. syriaca*. In addition, the two species formerly regarded as belonging to a neighbouring genus *Acerates* have a higher proportion of C₃₂ and C₃₃ alkanes than the others. Perhaps as additional work is done on other species in this genus the chemotaxonomic possibilities of the alkanes⁷ for these plants will emerge.

EXPERIMENTAL

Isolation of the alkanes The plants were collected in DeKalb and Ogle Counties, Illinois. Dried, powdered leaves and stems of each species were exhaustively extracted in a Soxhlet with hexane. The residue was reduced *in vacuo* and chromatographed on a column of Alcoa F-20 alumina. Elution with hexane gave the *n*-alkane mixture in the first 2 fractions. The absence of esters or other carbonyl containing compounds was verified by IR.

GLC analysis The alkane mixtures were analysed on a Varian-Aerograph Model 200 G C with a flame ionization detector connected to a Sargent SR recorder with a disc integrator. The instrument conditions used were as described in a previous report⁷ except the column temperature was programmed from 95–270° at a rate of 4–6° min. The peaks were identified by comparison to a reference mixture obtained as described below.

¹ For a review and leading references see B. SINGH and R. P. RASTOGI, *Phytochem* **9**, 315 (1970), R. ELBER, E. K. WEISS and T. REICHSTEIN, *Helv. Chim. Acta* **52**, 2583 (1969), H. MITSUHASHI, K. HAYASHI and K. TOMIMOTO, *Chem. Pharm. Bull.* **18**, 828 (1970).

² L. MARION, *Can. J. Res.* **17B**, 21 (1939).

³ Z. KOWALEWSKI and K. DROST, *Poznan Tow. Prayciaciol. Nauk, Wyd. Lek., Pr. Kom. Farm.* **5**, 75 (1966).

⁴ L. SCHMID and E. LUDWIG, *Monatsh. Chem.* **48**, 577 (1927).

⁵ A. E. RHEINECK, *Pharm. Arch.* **10**, 69, 93 (1939).

⁶ I. K. MATSUREVICH, *J. Appl. Chem. (U.S.S.R.)* **12**, 1730 (1939).

⁷ For reviews see A. G. DOUGLAS and G. EGLINTON, in *Comparative Phytochemistry* (edited by T. SWAIN), p. 57, Academic Press, London (1966), and G. EGLINTON and R. S. HAMILTON, in *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 187, Academic Press, London (1963).

The presence or absence of alkenes was determined by examining the peaks of the mixture before and after treatment with a few drops of Br_2 in CCl_4 . The data for each species are listed in Table 1.

Reference mixture The *n*-alkanes from *A. verticillata* were separated and collected with a Varian 90P G C. The detector was at 310° , the collector at 290° , the injection port at 300° , and the column at 210° for the C_{23} – C_{28} alkanes and at 235° for the C_{29} – C_{32} alkanes. A 5 ft 1/4 in. SS column packed with 3% SE-30 on 100/120 Varaport 30 and a helium flow rate of 60 ml/min were used.

Each individual peak was trapped in a capillary tube and subjected to mass spectral analysis. The formula for each alkane was obtained from the parent ion peak. The spectra were typical for *n*-alkanes and were devoid of any spurious peaks attributable to isoalkanes.

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Key Word Index—*Asclepias*, Asclepiadaceae, alkanes

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BIGNONIACEAE

CHRY SIN-7-RUTINOSIDE FROM THE LEAVES OF *DOLICHANDRONE FALCATA*

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Plant *Dolichandrone falcata* Seem. **Source.** Annamalai University Campus, South India. **Occurrence.** Distributed throughout India.¹ **Uses.** Medicinal.¹

Present work. Dried leaves extracted with 80% hot ethanol, and the aq. concentrate fractionated into petrol (40 – 60°), ether, EtOAc and MeCOEt.

Ether extract Luteolin (acetate, m.p. and mixed m.p.) and chrysin (R_f and co-chromatography with authentic samples).

TABLE 1. R_f s OF THE FLAVONOIDS OF *Dolichandrone falcata*

Flavonoid	R_f (Whatman No. 1, ascending $28 \pm 2^\circ$)							
	H_2O	15% HOAc	30% HOAc	60% HOAc	BAW	H_2O satd phenol	Forestral	TBA
Chrysin-7-rutinoside	12	29	53	76	40	70	83	68
Chrysin-7-glucoside	04	16	39	66	54	50	75	49
Chrysin	—	02	20	79	97	93	88	96

¹ *Wealth of India, Raw Materials*, Vol. III, p. 100, C S I R, New Delhi (1952).