*Present work.* Extraction of fresh leaves with hot 80% alcohol and fractionation into, (a) petrol (40–60°), (b) ether, (c) EtOAc, and (d) aq. mother liquor.

*Diosmetin* (*4'-methyl-luteolin*). (Ether fraction, $R_f$, m.p. and mixed m.p., $\lambda_{max}$, triaceate, m p. and mixed m.p , co-PC). *Diosmin* (*diosmetin-7-rhamnoglucoside*). (EtOAc fraction and aq. mother liquor after addition of $Me_2CO$), m p. 270–272° (dec ), $\lambda_{max}$ 253, 267, 334, $R_f$, acetate, m.p. 210° (earlier sintering at 125°), hydrolysis (10% $H_2SO_4$–HOAc = 1 1 refluxing for 5 hr) yielded diosmetin, glucose and rhamnose; partial hydrolysis (N.HCl, 100°, 5 min) yielded diosmetin-7-glucoside and rhamnose. *Diosmetin-7-glucoside.* (EtOAc and aq. mother liquor after addition of $Me_2CO$), m.p. 257–258° (dec.), $R_f$, hydrolysis (HOAc medium) yielded diosmetin and glucose, no separation on co-chromatography with diosmetin-7-glucoside obtained by partial hydrolysis of diosmin.

TABLE 1 $R_f$ OF THE FLAVONOIDS OF *Mentha spicata*

| Compound | $R_f$ (28°) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $H_2O$ | 15% HOAc | 30% HOAc | 60% HOAc | BAW | Forestal | $H_2O$-satd phenol |
| Diosmetin | 0.00 | 0.07 | 0.22 | 0.58 | 0.90 | 0.81 | 0.92 |
| Diosmin | 0.13 | 0.32 | 0.53 | 0.72 | 0.38 | 0.80 | 0.48 |
| Diosmetin-7-glucoside | 0.03 | 0.17 | 0.34 | 0.58 | 0.42 | 0.71 | 0.67 |

*Plant. Anisochilus carnosus* Wall.[3] *Uses.* Medicinal.[3] *Previous work.* None on flavonoids. *Present work.* Leaves. Extraction and fractionation as under *M spicata*

*Luteolin and apigenin* (*traces*). (Ether fraction—$R_f$, co-chromatography with authentic samples). *Luteolin-7-glucoside and apigenin-7-glucoside.* (EtOAc fraction—$R_f$, acid hydrolysis and co-chromatography). Luteolin-7-glucuronide and apigenin-7-glucuronide (EtOAc extract of the aq. mother liquor after acidification with dil. $H_2SO_4$) ($R_f$, solubility characteristics, resistance to hydrolysis with 7% $H_2SO_4$, hydrolysis with 10% $H_2SO_4$ in HOAc medium 5 hr and by β-glucuronidase to yield the aglycones and glucuronic acid, direct comparison and co-chromatography).

[3] *Wealth of India, Raw Materials*, Vol I, p 79, C S I R , New Delhi (1948)

*Key Word Index—Anisochilus carnosus, Mentha spicata*, Labiatae, flavones, diosmetin, luteolin, apigenin

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# IDENTIFICATION OF 5,9-DEHYDRONEPETALACTONE, A NEW MONOTERPENE FROM *NEPETA CATARIA**

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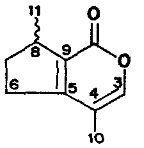
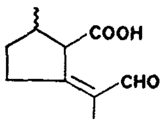
*Plant* *Nepeta cataria* (large leaf form) commonly called catnip. *Source.* During biosynthetic[1] studies of nepetalactone, an unusual plant having larger leaves (ranging from 3 to 5 in ) was observed among field grown *N. cataria* plants The large leaf type was further cultivated by making cuttings at the greenhouse of the Agricultural Experiment Station at Stillwater *Uses* Catnip plant is used as a feline sex attractant for cats.

*Isolation of* 5,9-*Dehydronepetalactone* (I) Fresh *N cataria* (large leaf type) plants (120 g) were ground and extracted four times with light petroleum Combined extracts were dried over $Na_2SO_4$ and concentrated to yield an oil (0 25%). 5,9-Dehydronepetalactone was isolated from the oil by preparative TLC in benzene–EtOAc (17 3) GLC analysis of the isolated lactone (I) showed a single peak on Apiezon L (15) coated on a Gas-Chrom-Q glass column.

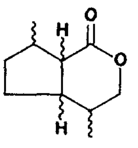
*Identification of* 5,9-*dehydronepetalactone* Characteristic IR bands at 1710 and 1640 $cm^{-1}$ indicated the presence of a conjugated carbonyl function The carbonyl group was found to be a conjugated lactone. When the lactone was treated with 2N KOH, it yields the acid aldehyde (II) NMR spectra of the lactone in $CDCl_3$ showed the following signals 2 92$\tau$ (singlet, 1H) due to a trisubstituted olefinic proton, 8 12$\tau$ (doublet, $J = 1$ c/s, 3H) due to a methyl group on an olefinic linkage and 8 8$\tau$ (doublet, $J = 7$ cps, 3H) due to a secondary methyl group High resolution mass spectra provided the mol wt of the compound as $m/e$ 164 with the analysis $C_{10}H_{12}O_2$ Catalytic hydrogenation of the lactone in ethanol in the presence of 10% Pd/C yielded the tetrahydrolactone (III, $M^+$ 168), which had a similar mass spectral fragmentation to that of dihydronepetalactone (IV) From the above experiments and spectral data, the lactone was assigned a cyclopentane monoterpenoid skeleton of the nepetalactone type with two double bonds as structure I



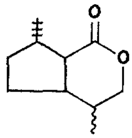
(I)



(II)



(III)



(IV)

An UV spectrum of the lactone (I) in ethanol had an absorption at 298 nm suggesting the presence of a pyrone[2] moiety, which is the conjugated lactone function with an extended conjugation From the NMR spectrum, the lactone consisted of one olefinic proton of the trisubstituted double bond Hence, the other double bond should be tetrasubstituted and in conjugation with the trisubstituted double bond The multiplet at 2 92$\tau$ can be assigned to the olefinic proton at C-3 of I One can visualize lactone (I) as a substituted $\alpha$-pyrone Further proof for the structure I is provided from the following experiments The lactone I after treatment with 10% KOH provided an acid aldehyde II which was immediately converted into a 2,4-dinitrophenylhydrazone (crude m p 105–107°) which showed the presence of a carbonyl function at 1720 $cm^{-1}$ due to the carboxyl group besides the characteristic absorption for the 2,4-dinitrophenylhydrazone moiety [3] From the above experiment, the location of the trisubstituted double bond in the lactone can be assigned at the C-3—C-4 position, since the lactone formed an acid aldehyde on the opening of the lactone ring.

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[1] F E REGNIER, G R WALLER, E J EISENBRAUN and H AUDA, *Phytochem* **7**, 221 (1968)

[2] J H ROSS, *Analyt Chem* **25**, 1288 (1953)

[3] L LANG, *Absorption Spectra in the UV and Visible Region*, Vol IV, p 636, Academic Press, New York (1963)

Now the location of the tetrasubstituted double bond is placed at the C-5—C-9 position in conjugation with the trisubstituted double bond thus making it α-pyrone moiety. From these data, Structure I is proposed for the new lactone

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*Key Word Index*—*Nepeta cataria*, Labiatae, monoterpene, 5,9-dehydronepetalactone.

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# CONSTITUENTS OF *ZATARIA MULTIFLORA**

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(*Received* 21 *April* 1971)

*Plant. Zataria multiflora*, Boiss. *Uses.* A reputed drug of the Unani system of medicine used as a stimulant, diaphoretic and diuretic, and for several other purposes[1] *Previous work* None, its essential oil (0 6%) studied in these laboratories consists of 69% phenols containing mainly carvacrol. *p*-Cymene is the main constituent of the non-phenolic portion of the oil[2]

*Extraction of the drug* The fragrant drug (leaves, stems and flowers) exhaustively extracted successively with light petroleum (60–80°), benzene, EtOH and MeOH and then the extracts repeatedly chromatographed on Silica gel (or alumina), and the products crystallized.

*New compounds* (Alkanes). Alkanes from earlier fractions of the neutral part of the petrol extract and crystallization (EtOH) (m p, mixed m p., IR, NMR, MS and GLC analysis): *n*-nonacosane ($C_{29}$), *n*-hentriacontane ($C_{31}$); *n*-dotriacontane ($C_{32}$); *n*-tritriacontane ($C_{33}$), *n*-pentatriacontane ($C_{35}$).

*β-Sitosterol* (m p, mixed m p. of the sterol and its acetate, IR, $[\alpha]_D$, and positive L B Test) Elution of the neutral part with benzene and crystallization (MeOH and $CHCl_3$) Benzoate (Found: C, 83 41; H, 9 91%, $C_{36}H_{54}O_2$ required: C, 83·34; H, 10·39%), 3 5-Dinitrobenzoate (Found· C, 71 47, H, 8 89, N, 5·09%, $C_{36}H_{52}O_6N_2$ required C, 71·02, H, 8 61, N, 4·6%)

*Betulin* (m p, IR, $[\alpha]_D$, $m/e$ 442 ($M^+$), positive L.B and Noller's Tests, co-TLC with authentic specimen) from $C_6H_6$–$CHCl_3$ (3 1) fractions of the neutral part and crystallization (ethyl-acetate). Its acetate (MeOH + acetone)· m p and IR

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* Major part of this work was presented at the "Convention of Chemists 1970" held at Madras (India) in Nov /Dec 1970

[1a] J Ch Sawer, *Odorographia, 2nd series*, p 148, Gurney & Jackson, London (1894)

[1b] R N Chopra, *Indigenous Drugs of India*, p 539 The Art Press, Calcutta (1933)

[1c] R N Chopra, S L Nayar and I C Chopra, *Glossdry of Indian Medicinal Plants*, p 260, C S I.R, New Delhi (1956)

[1d] W Dymock, C J H Warden and D. Hooper, *Pharmacographia Indica* **III**, 115 (1883)

[2a] G S Gupta and M O Farooq, *Perfumery and Essential Oil Record* **45**, 287 (1954).

[2b] G S Gupta and M O Farooq, *J & Proc Oil Tech Assn, India* **7**, 120 (1951).