oil. $[\alpha]_D$ −0.03° ($CHCl_3$; *c* 2.16); MS *m/z*: 218 $[M]^+$, 120, 83, 55; UV λ_{max}^{MeOH} nm (ε): 235.5 (21 100); IR ν_{max}^{film} cm^{-1}: 1680, 1615, 870; ^1H NMR ($CDCl_3$, 270 MHz): δ 0.88 (3H, *d*, *J* = 6.5 Hz, H-14), 1.88 and 2.14 (each 3H, *d*, *J* = 1.5 Hz, H-12 and H-13), 4.76 (2H, *br s*, H-15), 5.67 (1H, *br d*, *J* ≈ 10 Hz, H-2), 6.07 (1H, *m*, H-10), 6.17 (1H, *dd*, *J* = 10, 2 Hz, H-3); ^{13}C NMR ($CDCl_3$, 25 MHz): δ 16.5 (*q*), 20.7 (*q*), 25.0 (*t*), 27.7 (*q*), 30.1 (*t*), 33.3 (*d*), 40.5 (*d*), 48.6 (*t*), 110.3 (*t*), 124.1 (*d*), 130.0 (*d*), 133.7 (*d*), 143.3 (*s*), 154.9 (*s*), 200.7 (*s*).

Dehydrogenation of curlone. Curlone (20 mg) and Pd–C (5%, 20 mg) were heated at 320–340° for 3 min. The product in $CHCl_3$ was chromatographed on Si gel (20 g) to give (+)-*ar*-turmerone (8 mg) as a colourless oil. $[\alpha]_D$ + 54.0° ($CHCl_3$; *c* 0.25); MS *m/z*: 216 $[M]^+$, 201, 119, 83, 55; ^1H NMR ($CDCl_3$, 100 MHz): δ 1.24 (3H, *d*, *J* = 7 Hz), 1.84 (3H, *d*, *J* = 1 Hz), 2.10 (3H, *d*, *J* = 1 Hz), 2.29 (3H, *s*), 2.66 (2H, *m*), 3.29 (1H, *m*), 6.01 (1H, *m*), 7.07 (4H, *s*). Its identity was confirmed by the usual criteria.

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A FURANOEREMOPHILANE FROM *VITEX NEGUNDO**

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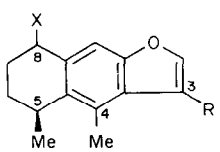
Key Word Index—*Vitex negundo*; Verbenaceae; roots; sesquiterpene; furanoeremophilane; 3-formyl-4,5-dimethyl-8-oxo-5*H*-6,7-dihydronaphtho(2,3-*b*)furan; acetyl oleanolic acid; sitosterol.

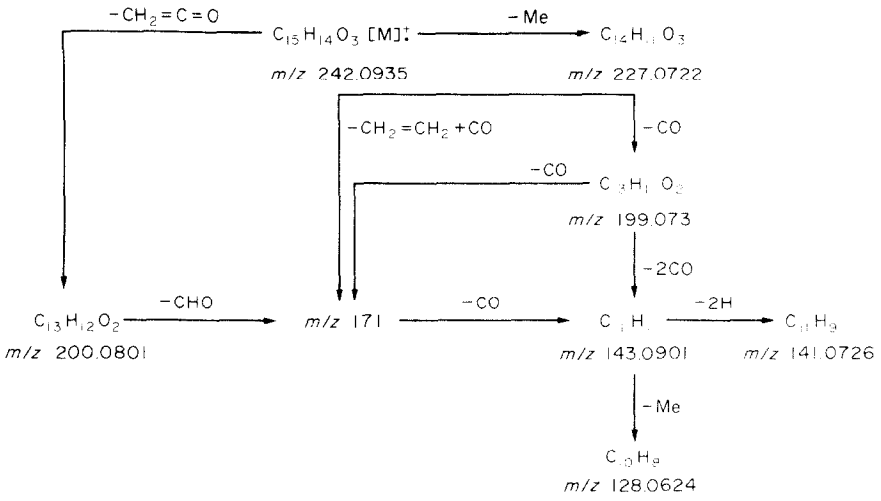
Abstract—Acetyl oleanolic acid, sitosterol and a new furanoeremophilane characterized as 3-formyl-4,5-dimethyl-8-oxo-5*H*-6,7-dihydronaphtho(2,3-*b*)furan have been isolated from the roots of *Vitex negundo*.

Vitex negundo, which is known for its antiarthritic activity in the indigenous system of medicine [1], has been extensively examined in the past to yield various constituents, such as, hydrocarbons [2], flavonoids [3], anthocyanins [4] and iridoids [5, 6]. As a continuation of our phytochemical investigations of medicinal plants, the benzene-soluble fraction of the ethanol extractives of *V. negundo* was examined to afford acetyl oleanolic acid, sitosterol and a new sesquiterpene, mp 145°, $[\alpha]_D^{20°}$ + 6.4° ($CHCl_3$; *c* 1.07%). The IR spectrum of the sesquiterpene exhibited the presence of PhCO and CHO functionalities (ν_{max}^{KBr} cm^{-1}: 1685 and 1700, respectively) together with bands characteristic of aromatic and furanoid moieties. The molecular composition, $C_{15}H_{14}O_3$, as determined by accurate mass measurements (M^+ at *m/z* 242.0935), indicated it to be a tricyclic sesquiterpene derivative. Further insight into its structure was gained by the study of its ^1H NMR spectrum which revealed the presence of 14 protons in agreement with the molecular composition. The low-field transitions consisted of three one-proton singlets identifiable as: (1) a formyl function (δ10.17); (2) C_2-H of a 3-formylbenzofuran moiety (δ8.40) [7]; and (3) the lone aromatic proton (δ8.10) situated peri to a C=O group [8]. A singlet which resonated at δ2.77 accounted for one aromatic methyl group while a second singlet at δ1.22 was identified as a secondary methyl group coupled with a benzylic methine (δ3.47) and confirmed by double resonance experiments. The remaining four protons were located at δ2.76 and 2.18 as multiplets pertaining to two CH_2 groups situated α- and β- to the carbonyl function, respectively. The preceding observations in conjunction with biogenetic concepts led to the characterization of this sesquiterpene as 3-formyl-4,5-dimethyl-8-oxo-5*H*-6,7-dihydronaphtho(2,3-*b*)furan (**1**). Reduction of **1** with sodium borohydride yielded a diol, $C_{15}H_{18}O_3$, M^+ at *m/z* 246. The carbonyl absorption bands of **1** were replaced by primary and secondary alcoholic functions in the IR spectrum of the diol. Besides the molecular ion, the rest of the electron impact mass spectral pattern was compatible with structure **2** for this diol.



	R	X
1	CHO	=O
2	CH_2OH	H, OH
3	Me	=O

*CDRI communication No. 3157. Part VIII in the series, "Studies in Medicinal Plants". For Part VII see, Rizvi, S. H., Shoeb, A., Kapil, R. S. and Popli, S. P. (1979) *Indian J. Pharm. Sci.* **41**, 205.



Scheme 1.

The proposed structure (**1**) was fully corroborated by the study of its high resolution mass spectrum (Scheme 1), the dominant features of which were the successive loss of all the three oxygen functions in the form of carbonyl groups to produce the benzocyclopropene ion [9] at *m/z* 143.0901 $[C_{11}H_{11}]^+$. The latter together with the dehydropropylium ion $[C_{11}H_9]^+$ derived from it are diagnostic spectral features of benzofuran derivatives, such as 2-formylbenzofuran [10] and furanocoumarins [11, 12]. The absolute stereochemistry was assigned to **1** on the basis of its ^{1}H NMR spectrum which was almost identical with that reported for desoxycacalol [8].

Sesquiterpenes with the modified eremophilane skeleton are common in the Compositae. The isolation of **1** constitutes the first example of the occurrence of such a compound in *V. negundo*. Biogenetically **1** appears to be the successor of 1-oxo-9-desoxycacalol (3,4,5-trimethyl-8-oxo-5*H*-6,7-dihydronaphtho(2,3-*b*)furan (**3**) which was recently isolated from *Senecio serratifolius* [8].

EXPERIMENTAL

All mps are uncorr. ^{1}H NMR spectra were recorded at 90 MHz using HMDS as internal standard and MS using direct inlet system.

Isolation of constituents. Air-dried powdered roots of *Vitex negundo* Linn. (20 kg) were extracted with 95% EtOH (3 × 20 l.) and the extract concd under red. pres. The residue (800 g) so obtained was diluted with H_2O (1 l.), defatted with hexane (4 × 1 l.) and extracted with C_6H_6 (4 × 1 l.). The C_6H_6-soluble residue (28 g) was chromatographed over Si gel (1.20 kg) and elution was effected with C_6H_6 followed by a mixture of C_6H_6 containing increasing proportions of EtOAc to afford **1** (25 mg), R_f 0.75 (TLC, Si gel, C_6H_6–EtOAc, 10:1); UV λ_{max}^{MeOH} nm (log ε): 230 (3.89) and 280 (4.17); IR ν_{max}^{KBr} cm^{-1}: 3135, 3065, 1700, 1685, 1570 and 1540. Further elution of the column gave acetyl oleanolic acid, mp 258°, M^+ *m/z* 498 (20 mg) and sitosterol, mp 136°, M^+ *m/z* 414 (2 g). A further quantity of **1** (15 mg) was isolated from the $CHCl_3$- soluble portion of the marc left after C_6H_6 extraction.

$NaBH_4$ *reduction of* **1**. A soln of **1** (10 mg) in MeOH (3 ml) was treated with $NaBH_4$ (50 mg) at 25° for 2 hr to furnish a viscous mass **2** (7 mg); IR ν_{max}^{KBr} cm^{-1}: 3450, 3400, 1580, 1480, 1460, 1260 and 1110; MS *m/z*: 246 $[M]^+$, 231, 204, 195, 183, 167, 128, 115 and 91.

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