

Chemical Constituents of *Impatiens balsamina* Linn.

AMARENDRA PATRA* and SWAPAN KUMAR CHAUDHURI

Department of Chemistry, University College of Science, 92 A. P. C. Road, Calcutta-700 009

Manuscript received 19 October 1987, revised 15 February 1988, accepted 19 February 1988

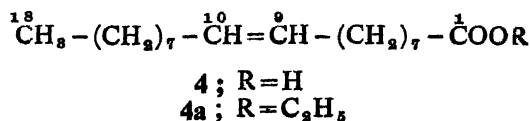
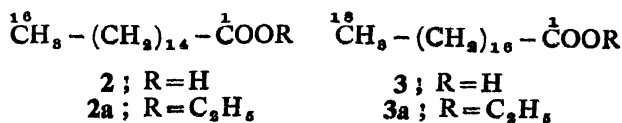
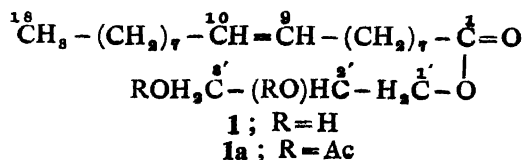
Chemical investigation on the seeds of *Impatiens balsamina* (Fam: Balsaminaceae) afforded a new monoglyceride (-)-(R,Z) glycerol 1-9-octadecenoate in addition to sitosterol, fatty esters (viz. ethyl palmitate, ethyl stearate and ethyl oleate) and fatty acids (viz. palmitic, stearic and oleic acids).

IMPATIENS balsamina Linn. (Fam: Balsaminaceae), an annual native of India, is now widely cultivated as an ornamental plant. The seeds of this plant have been used to treat difficult labour, to suppress puerperal pain, and to act as an emmenagogue, expectorant, and as an antidote for poisoning from fish in some oriental countries¹. Previous workers reported the isolation of viscous oil, β amyrin, α -spinasterol and balsamina sterol as unsaponifiable matters², sitosterol³, triholoside planteose⁴ and hosenkol-A⁵ from the seeds of the same plant. The present investigation on the seeds led to the isolation of a new monoglyceride (-)-(R,Z)-glycerol 1-9-octadecenoate (**1**) in addition to sitosterol, ethyl palmitate (**2a**), ethyl stearate (**3a**), ethyl oleate (**4a**), palmitic acid (**2**), stearic acid (**3**) and oleic acid (**4**). (-)-(R,Z)-Glycerol 1-9-octadecenoate (**1**), $C_{21}H_{40}O_4$, $[\alpha]_D^{25} -1.3^\circ$ ($CHCl_3$), had four oxygen atoms corresponding to ester function (ν_{max} 1730 and 1175 cm^{-1}) and hydroxyl groups (ν_{max} 3400 cm^{-1}) and had *cis*-olefinic function (ν_{max} 1650 and 720 cm^{-1} and positive TNM colour reaction). The ¹H nmr spectrum of **1** showed signals for a *cis*- $CH_2CH_2CH=CHCH_2CH_2-$ function at δ 5.34 (2H, t, *J* 4.5 Hz) and 2.00 (4H, m), a $-OCH_2CH(OH)CH_2OH$ moiety at δ 4.12 (2H, m, $H_{2-1'}$), 3.93 (1H, m, $H_{2-2'}$) and 3.63 (2H, m, $H_{2-3'}$) [the last two signals moved downfield in the spectrum of its diacetate (**1a**) (Ac_2O/Py) to δ 5.28 (1H, m, $H_{2-2'}$) and 4.17 (4H, m, $H_{2-1'}$ and $H_{2-3'}$)]. The downfield shifts (ca. 1.35 and 0.54 ppm) of $H_{2-2'}$ and $H_{2-3'}$ in **1a** relative to **1** supported the presence of secondary and primary alcoholic hydroxyls at C-2' and C-3'. The spectrum also exhibited resonances for a $-CH_2CH_2CO_2-$ group at δ 2.35 (2H, t, *J* 6.9 Hz), eleven CH_2 units at δ 1.27 (br, s) and a terminal CH_3CH_2 group at δ 0.88 (3H, t, *J* 6.0 Hz). These observations indicated the presence of an oleate moiety in **1**.

The above conclusions were supported from the ¹³C nmr spectrum of **1** and its diacetate **1a**. The ¹³C nmr spectrum of **1** revealed the presence of signals for a glyceryloxy moiety at δ 70.0 (C-2'), 64.8 (C-1') and 63.2 (C-3') and an oleate group at δ 174.0 (C-1), 129.7 (C-10 or C-9), 129.4 (C-9 or

C-10), 33.9 (C-2), 31.6 (C-16), 29.5 (C-4 and C-15), 29.3 (C-14), 29.0 (C-5 and C-13), 28.9 (C-6, C-7 and C-12), 26.9 (C-8 and C-11), 24.6 (C-3), 22.4 (C-17) and 13.8 (C-18) corroborating its molecular formula $C_{21}H_{40}O_4$. Its diacetate **1a** exhibited signals at δ 170.2 ($OCOCH_3$), 169.8 ($OCOCH_3$), 69.0 (C-2'), 62.1 (C-1'), 61.8 (C-3'), 20.4 ($2 \times OCOCH_3$) for the former moiety and at δ 173.0 (C-1), 129.8 and 129.5 (C-9 and C-10), 33.8 (C-2), 31.7 (C-16), 29.5 (C-5 and C-15), 29.3 (C-14), 29.1 (C-4 and C-13), 28.9 (C-6, C-7 and C-12), 27.0 (C-8 and C-11), 24.6 (C-3), 22.5 (C-17) and 13.9 (C-18) for the latter group. The upfield shifts (ca. 2.7, 1.4 and 1.0 ppm) of C-1', C-3' and C-2' resonances in **1a** relative to **1** were noted for γ -shielding effect as well as steric crowding of acetoxy functions. Hydrolysis of **1** with 2% methanolic KOH yielded oleic acid (**4**) identified by gas chromatography of the methyl ester and also by direct comparison with an authentic sample.

The above observations plus the ion fragments at *m/z* (%) 356 (M^+ , 10), 325 ($M^+ - CH_2OH$, 14), 295 ($M^+ - CHOHCH_2OH$, 6), 281 ($M^+ - CH_2CHOHCH_2OH$, 6), 265 ($M^+ - OCH_2CHOHCH_2OH$, 40), 264 ($M^+ - HOCH_2CHOHCH_2OH$, 100), 339 ($M^+ - OH$, 8) pointed to **1** being (-)-(R,Z)-glycerol 1-9-octadecenoate. This marks the first isolation of **1** from a natural source.



The fatty acids and ethyl esters were characterized from spectral studies and gas chromatographic analyses. Acid carbonyls absorbed at about 1700 cm^{-1} and the ester functions at 1738 and 1775 cm^{-1} . Compounds **4** and **4a** also had absorptions at 1650 and 725 cm^{-1} for *cis*-olefinic functions. The ^1H nmr spectra of **2**^a and **3**^a were similar and showed resonances at δ 2.35 (2H, t, J 6.7 Hz, CH_2COOH), 0.88 (3H, t, J 6.2 Hz, CH_2CH_3) as well as an intense peak at δ 1.26 [$-(\text{CH}_2)_n-$], while their ethyl esters **2a**^a and **3a**^a had additional resonances at δ 4.12 (2H, q, J 7.0 Hz) and 1.62 (3H, t, J 7.0 Hz). Compounds **4** and **4a**^a also showed ^1H nmr signals around δ 5.34 (2H, t, J 4.5 Hz, H -9 and H -10) and 2.00 (4H, m, allylic protons) as in **1**. Ethoxy carbons in **2a**-**4a** resonated at δ ~59.6 (CH_3) and 13.7 (CH_2), and esterification of the acids **2**-**4** led to upfield shift (~6.9 ppm) of the carbonyl resonance. Resonance positions of the various carbons in the oleate moiety in **1** and **4a** were comparable. Again, carbon spectrum of **2** was analogous to that of **3**. Mass spectra of **2**-**4** and **2a**-**4a** were typical of saturated and monounsaturated aliphatic acids and their ethyl esters as appropriate⁷.

The ethyl esters of fatty acids are considered to be artefacts formed during extraction with ethanol through solvolysis of glycerides by acyl hydrolase and lipases present in the live seeds. There is thus a possibility of **1** being similarly derived from a triglyceride.

Experimental

Ir spectra were run in neat, and ^1H nmr (80 MHz, TMS int. ref.) and ^{13}C nmr (20 MHz) spectra in CDCl_3 . Noise decoupling and APT experiments established carbon shifts and degree of protonation, the solvent serving as internal lock and internal standard ($\delta_{\text{TMS}} = \delta_{\text{CDCl}_3} + 76.9\text{ ppm}$). 10% DEGS and OV 1 columns were used for gas chromatographic analysis of fatty acids (as methyl esters) and their ethyl esters, respectively.

Isolation: Milled seeds of *Impatiens balsamina* (400 g) were extracted with EtOH at room temperature by percolation and concentrated under reduced pressure. The thick liquid residue (46 g) was chromatographed on silica gel (B.D.H., 60-120

mesh) and eluted with solvents and solvent mixtures of increasing polarity. Ethyl palmitate (**2a**; 0.203%), ethyl stearate (**3a**; 0.032%), ethyl oleate (**4a**; 0.015%), sitosterol (0.01%), palmitic acid (**2**; 0.10%), stearic acid (**3**; 0.012%), oleic acid (**4**; 0.006%) and $(-)-(R,Z)$ -glycerol 1-9-octadecenonate (**1**; 0.075%) were obtained after repeated column chromatography and then gas chromatography as required; *palmitic acid* (**2**): m.p. $38-40^\circ$ (CHCl_3 -MeOH); ^{13}C nmr δ 180.0 (C-1), 33.9 (C-2), 31.8 (C-14), 29.5 (C-4 to C-6, C-11 to C-13), 29.2 (C-7 and C-10), 28.9 (C-8 and C-9), 24.5 (C-3), 22.5 (C-15) and 13.9 (C-16); m/z (%) 256 (M^+ , 100), 228 (12), 227 (12), 213 (48), 199 (18), 196 (8), 185 (42), 171 (36), 157 (42), 143 (24), 129 (72), 115 (36), 101 (24), 87 (48) and 73 (72). The *diacetate* (**1a**): $[\alpha]_D^{25} \pm 0.0^\circ$ (CHCl_3); ν_{max} 1750, 1225 (ester $\text{O}=\text{C}-\text{O}$), 1650 and 725 cm^{-1} (*cis* $\text{C}=\text{C}$); ^1H nmr δ 5.28 (3H, m, H -9, H -10 and H -2'), 4.17 (4H, m, H_2 -1' and H_2 -3'), 2.31 (2H, t, J 6.9 Hz, H_2 -2), 2.06 (6H, s, $2 \times \text{OCOCH}_3$), 1.99 (4H, m, H_2 -8 and H_2 -11), 1.25 (22H, br s, $11 \times \text{CH}_2$) and 0.87 (3H, t, J 6.0 Hz, CH_2CH_3).

Acknowledgement

The authors are grateful to the U.G.C., New Delhi for financial assistance, to the Instrumentation Centre, C.A.S. on Natural Products, Department of Chemistry, University of Calcutta for ir and nmr spectra, to R.S.I.C., Bose Institute, Calcutta for mass spectra and to Dr. A. Ghosh, Bose Institute, Calcutta for gas chromatographic analyses.

References

1. L. M. PERRY, "Medicinal Plants of East and Southeast Asia", The MIT Press Cambridge 1980, p. 59.
2. B. MUKHERJEE and S. ROY, *Sci. Cult.*, 1956, **21**, 616.
3. S. P. DIKSHIT, *J. Oil Technol. Assoc. India*, 1973, **5**, 10.
4. A. D. YOUNG, J. E. CORROIS and P. L. DIZET, *C. R. Hebd. Seances Acad. Sci., Ser. D*, 1977, **285**, 1141.
5. N. SHOJI, A. UMEYAMA, Z. TAIRA, T. TAKEMOTO, K. NOMOTO, K. MIZUKAWA and Y. OHIZUMI, *J. Chem. Soc., Chem. Commun.*, 1988, 871.
6. "Handbook of Proton NMR Spectra and Data" ed. Asahi Research Centre Co., Academic, Tokyo, 1985, Vol. 5.
7. H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco 1964, p. 14.