3 components using  $C_6H_6$ -EtOAc (19 1) Component I  $R_1$  0.59 was bright yellow, co-chromatographed with propan-2-one DNP, MS 238 (M $^+$ ) MS was identical with that of pure propan-2-one DNP Component II  $R_1$  0.72 bright yellow, co-chromatographed with butanal DNP, MS 252 (M $^+$ ) The MS was identical with that of pure butanal DNP Component III  $R_1$  0.81, pale orange MS 306 (M $^+$ ) possibly the DNP of the unsaturated  $C_8$  aldehyde formed by aldol condensation of 2 molecules of butanal

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## REFERENCES

- 1 Reeves, R. J. and Jackson, R. M. (1972) Trans. Br. Mycol. Soc. 59, 156
- 2 Brasier, C M (1971) Nature, New Biology 231, 283
- 3 Pratt, B H, Sedgley, J H, Heather, W A and Shepherd, C J (1972) Aust J Biol Sci 25, 861
- 4 Collins R P and Halim. A F (1972) J Agr Food Chem 20, 437
- 5 Rey M. Dunkelblum E. Allain, R. and Dreiding, A. S. (1970) Heli. Chim. Acta 53, 2159

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## LIGNANS AND SUGIOL FROM LIBOCEDRUS BIDWILLII

## GRAFME B RUSSELL

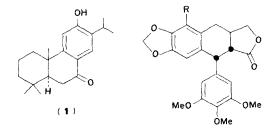
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**Key Word Index**—*Libocedrus bidwillii*, Cupressaceae, sugiol, deoxypodophyllotoxiii,  $\beta$ -peltatin-A methyl ether

Plant Libocedrus bidwillii Hook.f., common name, mountain ceder or pahautea Source Ruahine Ranges, State Forest 24, New Zealand. Previous work Terpenes of the essential oil [1-3]

Present work. Milled dried foliage (1.5 kg) was extracted with MeOH and the concentrate partitioned between light petroleum and MeOH- $H_2O$  (4.1) The aqueous phase was extracted with  $Et_2O$ , after removal of the MeOH, and the  $Et_2O$  fraction was chromatographed on an alumina column with  $C_6H_6$  followed by a silicic acid column with cyclohexane-EtOAc (4:1) This gave a series of fractions from which sugiol (1) mp  $287^\circ$ , deoxypodophyllotoxin [4,5] (2) mp  $166^{-168^\circ}$ ,  $[\alpha]_D - 114^\circ$  (CHCl<sub>3</sub>) and  $\beta$ -peltatin-4 methyl ether [6,7] (3) mp  $162^{-163^\circ}$   $[\alpha]_D - 119$ 



(2) R = H(3) R = OMe (CHCl<sub>3</sub>) were obtained crystalline. The identity of sugiol was established by direct comparison with authentic material (mmp IR, NMR, UV, MS) while the lignans were characterized from their IR, NMR, UV and MS [7,8]. Deoxypodophyllotoxin and  $\beta$ -peltatin-A methyl ether were refluxed in ethanolic sodium acetate for 18 hr to give their respective C-2 epimers. Deoxypicropodophyllin mp 171–172°,  $[\alpha]_D + 31$  (CHCl<sub>3</sub>), and  $\beta$ -peltatin- $\beta$  methyl ether mp 183–184°,  $[\alpha]_D + 9$ ° (CHCl<sub>3</sub>), were obtained in good yield

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## REFERENCES

- 1 Birrell K S (1932) J Soc Chem Ind Lond 51, 397T
- 2 Batt, R D and Slater, S N (1949) J Chem Soc 838
- 3 Aplin, R. T., Cambie, R. C. and Rutledge, P. S. (1963) Phytochemistry 2, 205
- 4 Hartwell, J L and Schrecker A W (1954) J Am Chem Soc 76, 4034
- 5 Kupchan S M, Hemingway, R J and Hemingway, J C. (1967) J Pharm Soc 56, 408
- 6 Hartwell, J. L. and Schrecker, A. W. (1952) J. Am. Chem. Soc. 74, 6285
- 7 Branchi, E., Sheth, K. and Cole, J. R. (1969) Tetrahedron Letters 2759
- 8 Hartwell, J. L. and Schrecker, A. W. (1958) Prog. Chem. Org. Nat. Prod. 15, 83