EXPERIMENTAL

Isolation of (+)-camphor and chamazulene. The title plant was collected in July, 1967 in Mt. Togakushi, Japan. The air-dried whole herbs (6 5 kg) were percolated with benzene (50 kg) at room temp. The extract was concentrated to 1 57 kg. A part (270 g) of the concentrated extract was steam-distilled. The distillate was extracted with benzene to give a blue benzene extract which was washed with 5% $NaHCO_3$ followed by H_2O. Evaporation of the solvent *in vacuo* gave a deep blue oil (4·7 g) which was distilled. A fraction, b.p $_4$ 40–60°, was purified by sublimation to give (+)-camphor, m.p. 180°. The blue fraction, b.p.$_4$ 90–110°, was converted to the TNB (trinitrobenzene) adduct. Crystallization from EtOH gave the TNB adduct of chamazulene, m.p. 133–134°.

Isolation of desacetylmatricarin and 'compound IIa' The concentrated benzene extract (1 3 kg) was evaporated and the residue (210 g) was extracted with *n*-hexane. The *n*-hexane insoluble powder (86 g) was chromatographed on silica gel (1 kg). The crystalline fractions eluted with benzene–ether (1:1) were combined and rechromatographed with benzene–EtOAc (1:1). The first eluate gave 2 1 g of I. (Found: C, 68·47; H, 6·85%.) Acetylation of I gave an acetate (II), m.p. 194–195°. II was identical to authentic matricarin by the standard methods. The second eluate gave 0 9 g of III. (Found: C, 68 51; H, 6·78%.) III was acetylated to give an acetate (IV), m.p 194–195°, $[\alpha]_D$ +137°. (Found: C, 67·39; H, 6·55%.)

Isomerization of desacetylmatricarin (I) A mixture of I (54 mg) and *tert*-BuOK (500 mg) in benzene (30 ml) was refluxed for 1 hr. The solution was acidified with 1 N H_2SO_4 and extracted with benzene. The organic layer was dried and evaporated. The residue was found to be the mixture of I (80%) and III (20%) by the analyses of NMR and TLC

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SENKIRKINE, A PYRROLIZIDINE ALKALOID FROM *FARFUGIUM JAPONICUM**

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Plant. Farfugium japonicum Kitam. (Tsuwabuki in Japanese)—tribe Senecioneae—Compositae.

Uses. Folk medicine for suppuration and eczema.[1]

Previous works. On the aldehydes[2] and phenolic products.[3]

THE MeOH EXTRACTS of the roots and leaves were shaken with 2 N H_2SO_4, respectively. Each acidic solution was reduced with zinc dust and filtered. The filtrate was made alkaline

* Part III in the series "Studies on Constituents of Crude Drugs". For Part II see T. FURUYA and M. HIKICHI, *Phytochem* **10,** 2217 (1971).

[1] T. KARIYONE and Y. KIMURA, *Wakan Yakuyoshokubutsu* (A Dictionary of Japanese and Chinese Medicinal Plants), p. 23, Hirokawa Publishing, Tokyo (1965).

[2] T. KOSUGE and M. YOKOTA, *Yakugaku Zasshi* **83,** 422 (1963).

[3] S. SAKAMURA, reported at *The 7th Symposium on Chemistry of Natural Phenolic Compounds*, Sendai, Japan (November 1970).

with ammonia and extracted with $CHCl_3$. The $CHCl_3$ solution was evaporated to obtain a crude alkaloid. Recrystallization from petroleum gave colorless needles, m.p. 197–198°, $[\alpha]_D^{25}$ −12° (EtOH), $C_{19}H_{27}O_6N$* which was estimated as senkirkine[4] from TLC, IR, NMR and mass spectral data and identical with the authentic sample by mixed m.p. and IR spectrum. The fresh roots (37 kg) and the dried leaves (3·65 kg) yielded 73 mg (0·0003%) and 130 mg (0·004%) of senkirkine, respectively.

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* Molecular formula was measured by high resolution mass spectrometer and the analytical value was in good agreement with the theoretical value.

[4] L. H. BRIGGS, R. C. CAMBIE, B. J. CANDY, G. M. O'DONOVAN, R. H. RUSSELL and R. N. SEELYE, *J. Chem. Soc.* 2492 (1965).

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ERICACEAE

LUPEOL AND β-SITOSTEROL IN *ARBUTUS MENZIESII**

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THE MOST abundant triterpenoid of *Arbutus menziesii*, betulinic acid, has already been reported.[1] Two other bark constituents have now been examined.

Benzene fractions from the silica gel chromatography reported in our previous communication[1] were rechromatographed over neutral alumina (activity 3), affording an intimate mixture of two substances. The two pure components were separated by acetylation of the mixture and a single chromatography (silica gel) of the resulting acetates. The first of the two pure components was a colorless solid, m.p. 212–213°, $[\alpha]_D^{25}$ + 33·4° (*c*. 0·981, $CHCl_3$). The mass spectrum of this component revealed a molecular ion peak at *m/e* 426 (426·3860); $C_{30}H_{50}O$ requires formula mass 426·3862. The cracking pattern, having intense

* Taken from the Honours B.Sc. Thesis of Thomas N. McCaig, University of Victoria (1969).

[1] FRANK P. ROBINSON, JR. and HENRI MARTEL, *Phytochem.* **9**, 907 (1970).