Anal. Calcd. for $C_{32}H_{34}O_6$: C, 74.68; H, 6.66; -CO-CH_3, 16.71; mol. wt., 514. Found: C, 74.88; H, 6.71; -$COCH_3$, 16.43; mol. wt., 488 ± 7 (Rast, in camphor).

Thymolphthalein Dimethyl Ether (VI).—4.3 g. (0.01 mole) of IV, 3.73 ml. (0.06 mole) of methyl iodide, 50 ml. of acetone and 2.76 g. (0.02 mole) of potassium carbonate were refluxed for ten hours. The crude was recrystallized from ethanol (1 g. in 24 ml.) yielding 4.03 g. (88%) of m. p. 175–176°. After two more crystallizations, it melted at 175.9–176.7°.[6]

(6) Lin Che Kin, *Ann. chim.*, **13**, 344 (1940), reports m. p. 177°. He prepared VI by condensing the methyl ether of thymol with the methyl ether of the 2-thymoylbenzoic acid in the presence of aluminum chloride.

Summary

Carvacrolphthalein was shown to melt at 294° and to be devoid of laxative effect. The melting point of 247° given in the literature for this compound is wrong. Thymolphthalein was prepared with a melting point 6° higher than reported heretofore. The diacetyl derivative and the dimethyl ether of both compounds were prepared.

BROOKLYN, N. Y. RECEIVED JULY 6, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, PURDUE UNIVERSITY AGRICULTURAL EXPERIMENT STATION]

Isolation of Lupeol from the Osage Orange (*Maclura pomifera* Raf.)[1]

BY LYLE JAMES SWIFT AND E. D. WALTER

In the isolation of osajin by Walter, Wolfrom and Hess[2] the dried osage oranges were first extracted with petroleum ether to remove latex and other interfering substances. In this paper the isolation of lupeol from this extract is described, and its crystallographic optical properties recorded. A wax-like material, to be described later, was also obtained.

Lupeol was discovered by Schulze[3] and described by Likiernik[4] and has since been isolated from several latex bearing plants. Ruzicka[5] recently proposed a structure for lupeol.

A characteristic reaction of lupeol is the red color it gives with concentrated sulfuric acid and acetic anhydride when in chloroform solution. This test also is given by the dried latex of the osage orange.

Acknowledgment.—We are indebted to Dr. M. L. Wolfrom, Department of Chemistry, Ohio State University for some of the extract used in this work.

Experimental

Isolation of Lupeol. The dried, ground osage oranges were completely extracted with low boiling petroleum ether. The extract was concentrated and passed through an aluminum silicate adsorbent described by Kraybill, *et al.*,[6] which removed the wax-like material. The concentrated petroleum ether extract was saponified with twice its volume of 95% ethanol saturated with potassium hydroxide. The mixture was diluted with water and extracted with ether. The ether was evaporated and the residue was mixed with about an equal weight of Nuchar W. The mixture was extracted in a Soxhlet apparatus with ether which was subsequently evaporated. Repeated crystallizations from acetone and then from 85% ethanol gave a product melting at 208–211°. Final purification was effected through formation of the acetate and saponification of this to get lupeol melting at 214–215°; yield, 5.1 g. of crude lupeol or 2.3 g. of pure lupeol from 1 kg. of dried osage oranges.

Anal. of lupeol. Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81; mol. wt., 426.7. Found: C, 84.45; H, 11.88; mol. wt. (freezing point depression using stearic acid), 448, 458; $[\alpha]^{22}D$ +27.63° ($CHCl_3$, c = 3.926). Ruzicka (7) obtained +27.2°.

Lupeol acetate was prepared by the method of Ruzicka[7]; yield, 1.88 g. (from 2.16 g. of lupeol) m. p. 216–216.5°. Ruzicka[7] reported a m. p. of 215–217°.

Anal. of lupeol acetate. Calcd. for $C_{30}H_{49}(OCOCH_3)$: C, 81.99; H, 11.18; mol. wt., 46.78. Found: C, 81.79; H, 11.29; mol. wt. (saponification equivalent), 469.5; $[\alpha]^{25}D$ +41.95° ($CHCl_3$, c = 1.652). Ruzicka obtained +40.7°.

Lupeol benzoate was prepared by the method of Ruzicka.[7] Lupeol (1.8 g.) yielded 1.57 g. of the benzoate m. p. 263–265°.

Anal. of lupeol benzoate. Calcd. for $C_{30}H_{49}(OCOC_6H_5)$: C, 83.72; H, 10.25; mol. wt., 530.8. Found: C, 83.59; H, 9.80; mol. wt. (saponification equivalent), 543; $[\alpha]^{25}D$ +61.36° ($CHCl_3$, c = 0.9908). Ruzicka obtained +60.9°.

(1) A portion of a thesis to be submitted by Lyle J. Swift to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Journal Paper No. 37, Purdue University Agricultural Experiment Station.

(2) E. D. Walter, M. L. Wolfrom and W. W. Hess, THIS JOURNAL, **60**, 574 (1938).

(3) E. Schulze and E. Steiger, *Landw. Vers.-Sta.*, **36**, 391 (1889).

(4) A. Likiernik, *Z. physiol. Chem.*, **15**, 415 (1891).

(5) L. Ruzicka and M. Brenner, *Helv. chim. acta.*, **23**, 1325 (1940).

(6) H. R. Kraybill, P. H. Brewer and M. H. Thornton, U. S. Patent No. 2,174,177, Sept. 26, 1939.

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Fig. 1.—Lupeol (×60).

Crystallographic Optical Properties

Lupeol.—In parallel polarized light (crossed nicols), the extinction is parallel; the elongation is negative. In convergent polarized light (crossed nicols) an optic normal interference figure is found on faces showing brightest white color. Refractive indices: n_α = 1.551, found lengthwise; n_β = indet.; n_γ = 1.565, found crosswise (both values ±0.003) (see Fig. 1).

Lupeol Acetate.—In parallel polarized light (crossed nicols) many faces show practically no extinction, while a few show red and blue interference colors and parallel extinction. In convergent polarized light (crossed nicols) a biaxial, optic axis figure is common. The optic sign is negative. Refractive indices: n_α = 1.540; n_β = 1.567 (both ±0.003); n_γ = indet.

Lupeol Benzoate.—In parallel polarized light (crossed nicols) the extinction is parallel; the elongation is negative. Many of the rods show red, green and yellow interference colors. In convergent polarized light (crossed nicols) biaxial interference figures are common. The optic sign is positive. Refractive indices: n_α = 1.565 found lengthwise on rods with red and blue interference colors; n_β = 1.567 found on fragments showing an optic axis interference figure; n_γ = 1.634 found crosswise, all ±0.003.

Summary

1. Lupeol has been isolated from the osage orange. Apparently it is a constituent of the latex.

2. Some crystallographic optical properties are presented for lupeol, lupeol acetate and lupeol benzoate.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

Surface Tensions, Densities and Parachors of the Aliphatic Nitroparaffins

BY G. E. BOYD AND L. E. COPELAND

Introduction

The synthesis and chemical properties of the aliphatic nitroparaffins previously have attracted considerable attention.[1-4] In view of the unusually high dipole moments shown (CH_3NO_2 = 3.13) by the molecules of these substances, it is of interest to determine the effect of this property upon the surface tension and the parachor. Since these liquids are extremely polar the possibility of two or more molecular species arises. Questions of this type sometimes may be settled by surface tension investigations.[5]

In the study reported, the variation of the surface tensions in the interval 25.0 to 60.0° of the first four members of the aliphatic nitroparaffins and their secondary isomers have been measured. Additionally, the variation of density with temperature, the total surface energies at 25°, the parachors and the critical temperatures have been obtained.

Apparatus, Chemicals and Methods

Reports of measurements of the variation of the surface tension with temperature are far less numerous in the literature than is to be desired. The variety of methods suitable is limited by a number of practical considerations. In these researches the ring method[3] was employed, and a clean liquid surface was insured by repeatedly overflowing the cup in which it was contained.

Although the question of technique and errors in the ring method has been discussed,[3,6] our experience has convinced us of the necessity of stressing certain vital points again.

If accurate results are to be obtained, it is essential that the ring be entirely in one plane, and that the stirrup supporting the ring be such that this plane be horizontal to a high degree of trueness. The effect of ring tilt has

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(3) W. D. Harkins and H. F. Jordan, THIS JOURNAL, **52**, 1751 (1930).

(4) H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

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(6) G. C. Nutting, F. A. Long and W. D. Harkins, THIS JOURNAL, **62**, 1496 (1940).